The Atomic Molecular Theory

Foundation

There are over 18 million known substances in our world. We will begin by assuming that all materials are made from **elements**, materials which cannot be decomposed into simpler substances. We will assume that we have identified all of these elements, and that there a very small number of them. All other pure substances, which we call **compounds**, are made up from these elements and can be decomposed into these elements. For example, metallic iron and gaseous oxygen are both elements and cannot be reduced into simpler substances, but iron rust, or ferrous oxide, is a compound which can be reduced to elemental iron and oxygen. The elements are not transmutable: one element cannot be converted into another. Finally, we will assume that we have demonstrated the **Law of Conservation of Mass**.
Law of Conservation of Mass

The total mass of all products of a chemical reaction is equal to the total mass of all reactants of that reaction. These statements are summaries of many observations, which required a tremendous amount of experimentation to achieve and even more creative thinking to systematize as we have written them here. By making these assumptions, we can proceed directly with the experiments which led to the development of the atomic-molecular theory.

Goals

The statements above, though correct, are actually more vague than they might first appear. For example, exactly what do we mean when we say that all materials are made from elements? Why is it that the elements cannot be decomposed? What does it mean to combine elements into a compound? We want to understand more about the nature of elements and compounds so we can describe the processes by which elements combine to form compounds, by which compounds are decomposed into elements, and by which compounds are converted from one to another during chemical reactions.

One possibility for answering these questions is to assume that a compound is formed when indestructible elements are simply mixed together, as for example, if we imagine stirring together a mixture of sugar and sand. Neither the sand nor the sugar is decomposed in the process. And the mixture can be decomposed back into the original components. In this case, though, the resultant mixture exhibits the properties of **both** components: for example, the mixture would taste sweet, owing to the sugar component, but gritty, characteristic of the sand component.

In contrast, the compound we call iron rust bears little resemblance to elemental iron: iron rust does not exhibit elemental iron's color, density, hardness, magnetism, etc. Since the properties of the elements are not maintained by the compound, then the compound must not be a simple mixture of the elements.

We could, of course, jump directly to the answers to these questions by stating that the elements themselves are comprised of atoms: indivisible, identical particles distinctive of that element. Then a compound is formed by combining the atoms of the composite elements. Certainly, the Law of Conservation of Mass would be easily explained by the existence of immutable atoms of fixed mass.

However, if we do decide to jump to conclusions and assume the existence of atoms without further evidence (as did the leading chemists of the seventeenth and eighteenth centuries), it does not lead us anywhere. What happens to iron when, after prolonged heating in air, it converts to iron rust? Why is it that the resultant combination of iron and air does not maintain the properties of either, as we would expect if the atoms of each are mixed together? An atomic view of nature would not yet provide any understanding of how the air and the iron have interacted or combined to form the new compound, and we can't make any predictions about how much iron will produce how much iron rust. There is no basis for making any statements about the properties of these atoms. We need further observations.

Observation 1: Mass relationships during chemical reactions

The Law of Conservation of Mass, by itself alone, does not require an atomic view of the elements. Mass could be conserved even if matter were not atomic. The importance of the Law of Conservation of Mass is that it reveals that we can usefully measure the masses of the elements which are contained in a fixed mass of a compound. As an example, we can decompose copper carbonate into its constituent elements, copper, oxygen, and carbon, weighing each and taking the ratios of these masses. The result is that every sample of copper carbonate is 51.5% copper, 38.8% oxygen, and 9.7% carbon. Stated differently, the masses of copper, oxygen, and carbon are in the ratio of 5.3 : 4 : 1, for every measurement of every sample of copper carbonate. Similarly, lead sulfide is 86.7% lead and 13.3% sulfur, so that the mass ratio for lead to sulfur in lead sulfide is always 6.5 : 1. Every sample of copper carbonate and every sample of lead sulfide will produce these elemental proportions, regardless of how much material we decompose or where the material came from. These results are examples of a general principle known as the **Law of Definite Proportions**.

Law of Definite Proportions

When two or more elements combine to form a compound, their masses in that compound are in a fixed and definite ratio.

These data help justify an atomic view of matter. We can simply argue that, for example, lead sulfide is formed by taking one lead atom and combining it with one sulfur atom. If this were true, then we also must conclude that the ratio of the mass of a lead **atom** to that of a sulfur **atom** is the same as the 6.5 : 1 lead to sulfur mass ratio we found for the bulk lead sulfide. This atomic explanation looks like the definitive answer to the question of what it means to combine two elements to make a compound, and it should even permit prediction of what quantity of lead sulfide will be produced by a given amount of lead. For example, 6.5g of lead will produce exactly 7.5g of lead sulfide, 50g of lead will produce 57.7g of lead sulfide, etc.

There is a problem, however. We can illustrate with three compounds formed from hydrogen, oxygen, and nitrogen. The three mass proportion measurements are given in the following table. First we examine nitric oxide, to find that the mass proportion is 8 : 7 oxygen to nitrogen. If this is one nitrogen atom combined with one oxygen atom, we would expect that the mass of an oxygen atom is 8/7=1.14 times that of a nitrogen atom. Second we examine ammonia, which is a combination of nitrogen and hydrogen with the mass proportion of 7 : 1.5 nitrogen to hydrogen. If this is one nitrogen combined with one hydrogen, we would expect that a nitrogen atom mass is 4.67 times that of a hydrogen atom mass. These two expectations predict a relationship between the mass of an oxygen atom and the mass of a hydrogen atom. If the mass of an oxygen atom is 1.14 times the mass of a nitrogen atom and if the mass of a nitrogen atom is 4.67 times the mass of a hydrogen atom, then we must conclude that an oxygen atom has a mass which is 1.14 × 4.67 = 5.34 times that of a hydrogen atom.

But there is a problem with this calculation. The third line of the following table shows that the compound formed from hydrogen and oxygen is water, which is found to have mass proportion 8:1 oxygen to hydrogen. Our expectation should then be that an oxygen atom mass is 8.0 times a hydrogen atom mass. Thus the three measurements in the following table appear to lead to contradictory expectations of atomic mass ratios. How are we to reconcile these results?

Compound	Total Mass	Mass of Hydrogen	Mass of Nitrogen	Mass of Oxygen	"Expected" Relative Atomic Mass of Hydrogen	"Expected" Relative Atomic Mass of Nitrogen	"Ex Rela Ato Mas Oxy
Nitric Oxide	15.0 g	-	7.0 g	8.0 g	-	7.0	8.0
Ammonia	8.5 g	1.5 g	7.0 g	-	1.5	7.0	-

Compound	Total Mass	Mass of Hydrogen	Mass of Nitrogen	Mass of Oxygen	"Expected" Relative Atomic Mass of Hydrogen	"Expected" Relative Atomic Mass of Nitrogen	"Ex Rela Ato Mas Oxy
Water	9.0 g	1.0 g	-	8.0 g	1.0	-	8.0

Mass Relationships for Hydrogen, Nitrogen, Oxygen Compounds

One possibility is that we were mistaken in assuming that there are atoms of the elements which combine to form the different compounds. If so, then we would not be surprised to see variations in relative masses of materials which combine.

Another possibility is that we have erred in our reasoning. Looking back, we see that we have to assume how many atoms of each type are contained in each compound to find the relative masses of the atoms. In each of the above examples, we assumed the ratio of atoms to be 1:1 in each compound. If there are atoms of the elements, then this assumption must be wrong, since it gives relative atomic masses which differ from compound to compound. How could we find the correct atomic ratios? It would help if we knew the ratio of the atomic masses: for example, if we knew that the oxygen to hydrogen mass ratio were 8:1, then we could conclude that the atomic ratio in water would be 1 oxygen and 1 hydrogen. Our reasoning seems to circular: to know the atomic masses, we must know the **formula** of the compound (the numbers of atoms of each type), but to know the formula we must know the masses.

Which of these possibilities is correct? Without further observations, we cannot say for certain whether matter is composed of atoms or not.

Observation 2: Multiple Mass Ratios

Significant insight into the above problem is found by studying different compounds formed from the same elements. For example, there are actually three oxides of nitrogen, that is, compounds composed only of nitrogen and oxygen. For now, we will call them oxide A, oxide B, and oxide C. Oxide A has oxygen to nitrogen mass ratio 2.28 : 1. Oxide B has oxygen to nitrogen mass ratio 1.14 : 1, and oxide C has oxygen to nitrogen mass ratio 0.57 : 1.

The fact that there are three mass ratios might seem to contradict the Law of Definite Proportions, which on the surface seems to say that there should be just one ratio. However, each mass combination gives rise to a completely unique chemical compound with very different chemical properties. For example, oxide A is very toxic, whereas oxide C is used as an anesthesia. It is also true that the mass ratio is not arbitrary or continuously variable: we cannot pick just any combination of masses in combining oxygen and nitrogen, rather we must obey one of only three. So there is no contradiction: we simply need to be careful with the Law of Definite Proportions to say **that each unique compound** has a definite mass ratio of combining elements.

These new mass ratio numbers are highly suggestive in the following way. Notice that, in each case, we took the ratio of oxygen mass to a nitrogen mass of 1, and that the resultant ratios have a very simple relationship:
Equation:

$$2.28 : 1.14 : 0.57 \;=\; 2 : 1 : 0.5$$
$$=\; 4 : 2 : 1$$

The masses of oxygen appearing in these compounds are in simple whole number ratios when we take a fixed amount of nitrogen. The appearance of these simple whole numbers is very significant. These integers imply that the compounds contain a multiple of a fixed unit of mass of oxygen. The simplest explanation for this fixed unit of mass is that oxygen is **particulate**. We call the fixed unit of mass an **atom**. We now assume that the compounds have been formed from combinations of atoms with fixed masses, and that different compounds have differing

numbers of atoms. The mass ratios make it clear that oxide B contains twice as many oxygen atoms (per nitrogen atom) as does oxide C and half as many oxygen atoms (per nitrogen atom) as does oxide A. The simple mass ratios must be the result of the simple ratios in which atoms combine into molecules. If, for example, oxide C has the molecular formula NO, then oxide B has the formula NO_2, and oxide A has the formula NO_4. There are other possibilities: if oxide B has molecular formula NO, then oxide A has formula NO_2, and oxide C has formula N_2O. Or if oxide A has formula NO, then oxide B has formula N_2O and oxide C has formula N_4O. These three possibilities are listed in the following table.

Assuming that:	Oxide C is NO	Oxide B is NO	Oxide A is NO
Oxide A is	NO_4	NO_2	NO
Oxide B is	NO_2	NO	N_2O
Oxide C is	NO	N_2O	N_4O

Possible Molecular Formulae for Nitrogen Oxides

We don't have a way (from these data) to know which of these sets of molecular formulae are right. But we can assert that either one of them or one analogous to them is right.

Similar data are found for any set of compounds formed from common elements. For example, there are two oxides of carbon, one with oxygen to carbon mass ratio 1.33:1 and the other with mass ratio 2.66:1. The second oxide must have twice as many oxygen atoms, per carbon atom, as does the first. The general statement of this observation is the **Law of Multiple Proportions**.
Law of Multiple Proportions

When two elements combine to form more than one compound, the mass of element A which combines in the first compound with a given amount of element B has a simple whole number ratio with the mass of element A which combines in the second compound with the same given mass of element B.
This sounds confusing, but an example clarifies this statement. Consider the carbon oxides, and let carbon be element B and oxygen be element A. Take a fixed given mass of carbon (element B), say 1 gram. The mass of oxygen which combines with 1 gram of carbon to form the first oxide is 1.33 grams. The mass of oxygen which combines with 1 gram of carbon to form the second oxide is 2.66. These masses are in ratio $2.66 : 1.33 = 2 : 1$, a simple whole number ratio.

In explaining our observations of the Law of Multiple Proportions for the carbon oxides and the nitrogen oxides, we have concluded that the simple mass ratio arises from the simple ratio of atoms contained in the individual molecules. Thus, we have established the following postulates of the **Atomic Molecular Theory**.
TheoryAtomic Molecular Theory

- the elements are comprised of identical atoms
- all atoms of a single element have the same characteristic mass
- these number and masses of these atoms do not change during a chemical transformation
- compounds consist of identical molecules formed of atoms combined in simple whole number ratios

Review and Discussion Questions

Exercise:

Problem:

Assume that matter does not consist of atoms. Show by example how this assumption leads to hypothetical predictions which contradict the Law of Multiple Proportions. Do these hypothetical examples contradict the Law of Definite Proportions? Are both observations required for confirmation of the atomic theory?

Exercise:

Problem:

Two compounds, A and B, are formed entirely from hydrogen and carbon. Compound A is 80.0% carbon by mass, and 20.0% hydrogen, whereas Compound B is 83.3% carbon by mass and 16.7% hydrogen. Demonstrate that these two compounds obey the Law of Multiple Proportions. Explain why these results strongly indicate that the elements carbon and hydrogen are composed of atoms.

Exercise:

Problem:

In many chemical reactions, mass does not appear to be a conserved quantity. For example, when a tin can rusts, the resultant rusty tin can has a greater mass than before rusting. When a candle burns, the remaining candle has invariably less mass than before it was burned. Provide an explanation of these observations, and describe an experiment which would demonstrate that mass is actually conserved in these chemical reactions.

Exercise:

Problem:

The following question was posed on an exam:"An unknown non-metal element (Q) forms two gaseous fluorides of unknown molecular formula. A 3.2 g sample of Q reacts with fluorine to form 10.8 g of the unknown fluoride A. A 6.4 g sample of Q reacts with fluorine to form 29.2 g of unknown fluoride B. Using these data only, demonstrate by calculation and explanation that these unknown compounds obey the Law of Multiple Proportions."A student responded with the following answer:"The Law of Multiple Proportions states that when two elements form two or more compounds, the ratios of the masses of the elements between the two compounds are in a simple whole number ratio. So, looking at the data above, we see that the ratio of the mass of element Q in compound A to the mass of element Q in compound B is $3.2 : 6.4 = 1 : 2$, which is a simple whole number ratio. This demonstrates that these compounds obey the Law of Multiple Proportions."Assess the accuracy of the students answer. In your assessment, you must determine what information is correct or incorrect, provide the correct information where needed, explain whether the reasoning is logical or not, and provide logical reasoning where needed.

Relative Atomic Masses and Empirical Formulae

Foundation

We begin by assuming the central postulates of the **Atomic-Molecular Theory**. These are: the elements are comprised of identical atomsall atoms of a single element have the same characteristic massthe number and masses of these atoms do not change during a chemical transformation compounds consist of identical molecules formed of atoms combined in simple whole number ratios. We also assume a knowledge of the observed natural laws on which this theory is based: the **Law of Conservation of Mass**, the **Law of Definite Proportions**, and the **Law of Multiple Proportions**.

Goals

We have concluded that atoms combine in simple ratios to form molecules. However, we don't know what those ratios are. In other words, we have not yet determined any molecular formulae. In [the second table of Concept Development Study #1](), we found that the mass ratios for nitrogen oxide compounds were consistent with many different molecular formulae. A glance back at the nitrogen oxide data shows that the oxide B could be NO, NO_2, N_2O, or any other simple ratio.

Each of these formulae correspond to different possible relative atomic weights for nitrogen and oxygen. Since oxide B has oxygen to nitrogen ratio 1.14 : 1, then the relative masses of oxygen to nitrogen could be 1.14:1 or 2.28:1 or 0.57:1 or many other simple possibilities. If we knew the relative masses of oxygen and nitrogen atoms, we could determine the molecular formula of oxide B. On the other hand, if we knew the molecular formula of oxide B, we could determine the relative masses of oxygen and nitrogen atoms. If we solve one problem, we solve both. Our problem then is that we need a simple way to "count" atoms, at least in relative numbers.

Observation 1: Volume Relationships in Chemical Reactions

Although mass is conserved, most chemical and physical properties are not conserved during a reaction. Volume is one of those properties which is not

conserved, particularly when the reaction involves gases as reactants or products. For example, hydrogen and oxygen react explosively to form water vapor. If we take 1 liter of oxygen gas and 2 liters of hydrogen gas, by careful analysis we could find that the reaction of these two volumes is complete, with no left over hydrogen and oxygen, and that 2 liters of water vapor are formed. Note that the total volume is not conserved: 3 liters of oxygen and hydrogen become 2 liters of water vapor. (All of the volumes are measured at the same temperature and pressure.)

More notable is the fact that the ratios of the volumes involved are simple whole number ratios: 1 liter of oxygen : 2 liters of hydrogen : 2 liters of water. This result proves to be general for reactions involving gases. For example, 1 liter of nitrogen gas reacts with 3 liters of hydrogen gas to form 2 liters of ammonia gas. 1 liter of hydrogen gas combines with 1 liter of chlorine gas to form 2 liters of hydrogen chloride gas. These observations can be generalized into the **Law of Combining Volumes**.
Law of Combining Volumes

When gases combine during a chemical reaction at a fixed pressure and temperature, the ratios of their volumes are simple whole number ratios.

These simple integer ratios are striking, particularly when viewed in the light of our conclusions from the Law of Multiple Proportions. Atoms combine in simple whole number ratios, and evidently, volumes of gases also combine in simple whole number ratios. Why would this be? One simple explanation of this similarity would be that the volume ratio and the ratio of atoms and molecules in the reaction are the same. In the case of the hydrogen and oxygen, this would say that the ratio of volumes (1 liter of oxygen : 2 liters of hydrogen : 2 liters of water) is the same as the ratio of atoms and molecules (1 atom of oxygen: 2 atoms of hydrogen: 2 molecules of water). For this to be true, equal volumes of gas would have to contain equal numbers of gas particles (atoms or molecules), independent of the type of gas. If true, this means that the volume of a gas must be a direct measure of the number of particles (atoms or molecules) in the gas. This would allow us to "count" the number of gas particles and determine molecular formulae.

There seem to be big problems with this conclusion, however. Look back at the data for forming hydrogen chloride: 1 liter of hydrogen plus 1 liter of

chlorine yields 2 liters of hydrogen chloride. If our thinking is true, then this is equivalent to saying that 1 hydrogen atom plus 1 chlorine atom makes 2 hydrogen chloride molecules. But how could that be possible? How could we make 2 identical molecules from a single chlorine atom and a single hydrogen atom? This would require us to divide each hydrogen and chlorine atom, violating the postulates of the atomic-molecular theory.

Another problem appears when we weigh the gases: 1 liter of oxygen gas weighs more than 1 liter of water vapor. If we assume that these volumes contain equal numbers of particles, then we must conclude that 1 oxygen particle weighs more than 1 water particle. But how could that be possible? It would seem that a water molecule, which contains at least one oxygen atom, should weigh more than a single oxygen particle.

These are serious objections to the idea that equal volumes of gas contain equal numbers of particles. Our postulate appears to have contradicted common sense and experimental observation. However, the simple ratios of the Law of Combining Volumes are also equally compelling. Why should volumes react in simple whole number ratios if they do not represent equal numbers of particles? Consider the opposite viewpoint: if equal volumes of gas do not contain equal numbers of particles, then equal numbers of particles must be contained in unequal volumes not related by integers. Now when we combine particles in simple whole number ratios to form molecules, the volumes of gases required would produce decidedly non-whole number ratios. The Law of Combining Volumes should not be contradicted lightly.

There is only one logical way out. We will accept our deduction from the Law of Combining Volumes that **equal volumes of gas contain equal numbers of particles**, a conclusion known as **Avogadro's Hypothesis**. How do we account for the fact that 1 liter of hydrogen plus 1 liter of chlorine yields 2 liters of hydrogen chloride? There is only one way for a single hydrogen particle to produce 2 identical hydrogen chloride molecules: each hydrogen particle must contain more than one atom. In fact, each hydrogen particle (or molecule) must contain an even number of hydrogen atoms. Similarly, a chlorine molecule must contain an even number of chlorine atoms.

More explicitly, we observe that
Equation:

1 liter of hydrogen + 1 liter of chlorine → 2 liters of hydrogen chloride

Assuming that each liter volume contains an equal number of particles, then we can interpret this observation as
Equation:

$$1\,H_2\text{molecule} + 1\,Cl_2\,\text{molecule} \rightarrow 2\,H\,Cl\,\text{molecules}$$

(Alternatively, there could be any fixed even number of atoms in each hydrogen molecule and in each chlorine molecule. We will assume the simplest possibility and see if that produces any contradictions.)

This is a wonderful result, for it correctly accounts for the Law of Combining Volumes and eliminates our concerns about creating new atoms. Most importantly, we now know the molecular formula of hydrogen chloride. We have, in effect, found a way of "counting" the atoms in the reaction by measuring the volume of gases which react.

This method works to tell us the molecular formula of many compounds. For example,
Equation:

$$2\text{ liters of hydrogen} + 1\text{ liter of oxygen} \rightarrow 2\text{ liters of water}$$

This requires that oxygen particles contain an even number of oxygen atoms. Now we can interpret this equation as saying that
Equation:

$$2\,H_2\text{molecules} + 1\,O_2\text{molecule} \rightarrow 2\,H_2O\,\text{molecules}$$

Now that we know the molecular formula of water, we can draw a definite conclusion about the relative masses of the hydrogen and oxygen atoms. Recall from the Table that the mass ratio in water is 8:1 oxygen to hydrogen.

Since there are two hydrogen atoms for every oxygen atom in water, then the mass ratio requires that a single oxygen atom weigh 16 times the mass of a hydrogen atom.

To determine a mass scale for atoms, we simply need to choose a standard. For example, for our purposes here, we will say that a hydrogen atom has a mass of 1 on the atomic mass scale. Then an oxygen atom has a mass of 16 on this scale.

Our conclusions account for the apparent problems with the masses of reacting gases, specifically, that oxygen gas weighs more than water vapor. This seemed to be nonsensical: given that water contains oxygen, it would seem that water should weigh more than oxygen. However, this is now simply understood: a water molecule, containing only a single oxygen atom, has a mass of 18, whereas an oxygen molecule, containing two oxygen atoms, has a mass of 32.

Determination of Atomic Weights for Gaseous Elements

Now that we can count atoms and molecules to determine molecular formulae, we need to determine relative atomic weights for all atoms. We can then use these to determine molecular formulae for any compound from the mass ratios of the elements in the compound.

We begin by examining data on reactions involving the Law of Combining Volumes. Going back to the nitrogen oxide data given here, we recall that there are three compounds formed from nitrogen and oxygen. Now we measure the volumes which combine in forming each. We find that 2 liters of oxide B can be decomposed into 1 liter of nitrogen and 1 liter of oxygen. From the reasoning above, then a nitrogen particle must contain an even number of nitrogen atoms. We assume for now that nitrogen is N_2. We have already concluded that oxygen is O_2. Therefore, the molecular formula for oxide B is NO, and we call it nitric oxide. Since we have already determined that the oxygen to nitrogen mass ratio is 1.14 : 1, then, if we assign oxygen a mass of 16, as above, nitrogen has a mass of 14. (That is $\frac{16}{1.14} = 14$.) 2 liters of oxide A is formed from 2 liters of oxygen and 1 liter of nitrogen. Therefore, oxide A is NO_2, which we call nitrogen dioxide. Note that we

predict an oxygen to nitrogen mass ratio of $\frac{32}{14} = 2.28 : 1$, in agreement with the data. Oxide C is N_2O, called nitrous oxide, and predicted to have a mass ratio of $\frac{16}{28} = 0.57 : 1$, again in agreement with the data. We have now resolved the ambiguity in the molecular formulae.

What if nitrogen were actually N_4? Then the first oxide would be N_2O, the second would be N_2O_2, and the third would be N_4O. Furthermore, the mass of a nitrogen atom would be 7. Why don't we assume this? Simply because in doing so, we will always find that the minimum relative mass of nitrogen in any molecule is 14. Although this might be two nitrogen atoms, there is no reason to believe that it is. Therefore, a single nitrogen atom weighs 14, and nitrogen gas particles are N_2.

Determination of Atomic Weights for Non-Gaseous Elements

We can proceed with this type of measurement, deduction, and prediction for any compound which is a gas and which is made up of elements which are gases. But this will not help us with the atomic masses of non-gaseous elements, nor will it permit us to determine the molecular formulae for compounds which contain these elements.

Consider carbon, an important example. There are two oxides of carbon. Oxide A has oxygen to carbon mass ratio 1.33 : 1 and oxide B has mass ratio 2.66 : 1. Measurement of reacting volumes shows that we find that 1 liter of oxide A is produced from 0.5 liters of oxygen. Hence, each molecule of oxide A contains only half as many oxygen atoms as does an oxygen molecule. Oxide A thus contains one oxygen atom. But how many carbon atoms does it contain? We can't determine this yet because the elemental carbon is solid, not gas. This means that we also cannot determine what the mass of a carbon atom is.

But we can try a different approach: we weigh 1 liter of oxide A and 1 liter of oxygen gas. The result we find is that oxide A weighs 0.875 times per liter as much as oxygen gas. Since we have assumed that a fixed volume of gas contains a fixed number of particles, then 1 liter of oxide A contains just as many particles as 1 liter of oxygen gas. Therefore, each **particle** of oxide A weighs 0.875 times as much as a particle of oxygen gas (that is, an O_2

molecule). Since an O_2 molecule weighs 32 on our atomic mass scale, then a particle of oxide A weighs $0.875 \times 32 = 28$. Now we know the molecular weight of oxide A.

Furthermore, we have already determined from the combining volumes that oxide A contains a single oxygen atom, of mass 16. Therefore, the mass of carbon in oxide A is 12. However, at this point, we do not know whether this is one carbon atom of mass 12, two atoms of mass 6, eight atoms of mass 1.5, or one of many other possibilities.

To make further progress, we make additional measurements on other carbon containing gas compounds. 1 liter of oxide B of carbon is formed from 1 liter of oxygen. Therefore, each oxide B molecule contains two oxygen atoms. 1 liter of oxide B weighs 1.375 times as much as 1 liter of oxygen. Therefore, one oxide B molecule has mass $1.375 \times 32 = 44$. Since there are two oxygen atoms in a molecule of oxide B, the mass of oxygen in oxide B is 32. Therefore, the mass of carbon in oxide B is 12, the same as in oxide A.

We can repeat this process for many such gaseous compounds containing carbon atoms. In each case, we find that the mass of carbon in each molecule is either 12 or a multiple of 12. We never find, for examples, 6 or 18, which would be possible if each carbon atom had mass 6. The simplest conclusion is that a carbon atom has mass 12. Once we know the atomic mass of carbon, we can conclude that the molecular formula of oxide A is CO, and that of oxide B is CO_2.

Therefore, the atomic masses of non-gaseous elements can be determined by mass and volume measurements on gaseous compounds containing these elements. This procedure is fairly general, and most atomic masses can be determined in this way.

Moles, Molecular Formulae and Stoichiometric Calculations

We began with a circular dilemma: we could determine molecular formulae provided that we knew atomic masses, but that we could only determine atomic masses from a knowledge of molecular formulae. Since we now have a method for determining all atomic masses, we have resolved this dilemma

and we can determine the molecular formula for any compound for which we have percent composition by mass.

As a simple example, we consider a compound which is found to be 40.0% carbon, 53.3% oxygen, and 6.7% hydrogen by mass. Recall from the Law of Definite Proportions that these mass ratios are independent of the sample, so we can take any convenient sample to do our analysis. Assuming that we have 100.0g of the compound, we must have 40.0g of carbon, 53.3g of oxygen, and 6.7g of hydrogen. If we could count or otherwise determine the number of atoms of each element represented by these masses, we would have the molecular formula. However, this would not only be extremely difficult to do but also unnecessary.

From our determination of atomic masses, we can note that 1 atom of carbon has a mass which is 12.0 times the mass of a hydrogen atom. Therefore, the mass of N atoms of carbon is also 12.0 times the mass of N atoms of hydrogen atoms, no matter what N is. If we consider this carefully, we discover that 12.0g of carbon contains exactly the same number of atoms as does 1.0g of hydrogen. Similarly, we note that 1 atom of oxygen has a mass which is $\frac{16.0}{12.0}$ times the mass of a carbon atom. Therefore, the mass of N atoms of oxygen is $\frac{16.0}{12.0}$ times the mass of N atoms of carbon. Again, we can conclude that 16.0g of oxygen contains exactly the same number of atoms as 12.0g of carbon, which in turn is the same number of atoms as 1.0g of hydrogen. Without knowing (or necessarily even caring) what the number is, we can say that it is the same number for all three elements.

For convenience, then, we **define** the number of atoms in 12.0g of carbon to be 1 **mole** of atoms. Note that 1 mole is a specific number of particles, just like 1 dozen is a specific number, independent of what objects we are counting. The advantage to defining the mole in this way is that it is easy to determine the number of moles of a substance we have, and knowing the number of moles is equivalent to counting the number of atoms (or molecules) in a sample. For example, 24.0g of carbon contains 2.0 moles of atoms, 30.0g of carbon contains 2.5 moles of atoms, and in general, x grams of carbon contains $\frac{x}{12.0}$ moles of atoms. Also, we recall that 16.0g of oxygen contains exactly as many atoms as does 12.0g of carbon, and therefore 16.0g of oxygen contains exactly 1.0 mole of oxygen atoms. Thus, 32.0g of

oxygen contains 2.0 moles of oxygen atoms, 40.0g of oxygen contains 2.5 moles, and x grams of oxygen contains $\frac{x}{16.0}$ moles of oxygen atoms. Even more generally, then, if we have m grams of an element whose atomic mass is M, the number of moles of atoms, n, is

Equation:

$$n = \frac{m}{M}$$

Now we can determine the relative numbers of atoms of carbon, oxygen, and hydrogen in our unknown compound above. In a 100.0g sample, we have 40.0g of carbon, 53.3g of oxygen, and 6.7g of hydrogen. The number of moles of atoms in each element is thus

Equation:

$$
\begin{aligned}
n_C &= \frac{40.0g}{12.0\frac{g}{\text{mol}}} \\
&= 3.33\,\text{moles}
\end{aligned}
$$

Equation:

$$
\begin{aligned}
n_O &= \frac{53.3g}{16.0\frac{g}{\text{mol}}} \\
&= 3.33\,\text{moles}
\end{aligned}
$$

Equation:

$$
\begin{aligned}
n_H &= \frac{6.7g}{1.0\frac{g}{\text{mol}}} \\
&= 6.67\,\text{moles}
\end{aligned}
$$

We note that the numbers of moles of atoms of the elements are in the simple ratio $n_C : n_O : n_H = 1 : 1 : 2$. Since the number of particles in 1 mole is the same for all elements, then it must also be true that the number of atoms of the elements are in the simple ratio $1 : 1 : 2$. Therefore, the molecular formula of the compound must be COH_2.

Or is it? On further reflection, we must realize that the simple ratio $1:1:2$ need not represent the exact numbers of atoms of each type in a molecule of the compound, since it is indeed only a ratio. Thus the molecular formula could just as easily be $C_2O_2H_4$ or $C_3O_3H_6$. Since the formula COH_2 is based on empirical mass ratio data, we refer to this as the **empirical formula** of the compound. To determine the **molecular formula**, we need to determine the relative mass of a molecule of the compound, i.e. the molecular mass. One way to do so is based on the Law of Combining Volumes, Avogadro's Hypothesis, and the **Ideal Gas Law**. To illustrate, however, if we were to find that the relative mass of one molecule of the compound is 60.0, we could conclude that the molecular formula is $C_2O_2H_4$.

Review and Discussion Questions

Exercise:

  Problem:

  State the Law of Combining Volumes and provide an example of your own construction which demonstrates this law.

Exercise:

  Problem:

  Explain how the Law of Combining Volumes, combined with the Atomic-Molecular Theory, leads directly to Avogadro's Hypothesis that equal volumes of gas at equal temperatures and pressure contain equal numbers of particles.

Exercise:

  Problem:

  Use Avogadro's Hypothesis to demonstrate that oxygen gas molecules cannot be monatomic.

Exercise:

Problem:

The density of water vapor at room temperature and atmospheric pressure is $0.737\frac{g}{L}$. Compound A is 80.0% carbon by mass, and 20.0% hydrogen. Compound B is 83.3% carbon by mass and 16.7% hydrogen. The density of gaseous Compound A is $1.227\frac{g}{L}$, and the density of Compound B is $2.948\frac{g}{L}$. Show how these data can be used to determine the molar masses of Compounds A and B, assuming that water has molecular mass 18.

Exercise:

Problem:

From the results above, determine the mass of carbon in a molecule of Compound A and in a molecule of Compound B. Explain how these results indicate that a carbon atom has atomic mass 12.

Exercise:

Problem:

Explain the utility of calculating the number of moles in a sample of a substance.

Exercise:

Problem:

Explain how we can conclude that 28g of nitrogen gas (N_2) contains exactly as many molecules as 32g of oxygen gas (O_2), even though we cannot possibly count this number.

The Structure of an Atom

Foundation

We begin as a starting point with the atomic molecular theory. We thus assume that most of the common elements have been identified, and that each element is characterized as consisting of identical, indestructible atoms. We also assume that the atomic weights of the elements are all known, and that, as a consequence, it is possible via mass composition measurements to determine the molecular formula for any compound of interest. In addition, we will assume that it has been shown by electrochemical experiments that atoms contain equal numbers of positively and negatively charged particles, called protons and electrons respectively. Finally, we assume an understanding of the Periodic Table. In particular, we assume that the elements can be grouped according to their common chemical and physical properties, and that these chemical and physical properties are periodic functions of the atomic number.

Goals

The atomic molecular theory is extremely useful in explaining what it means to form a compound from its component elements. That is, a compound consists of identical molecules, each comprised of the atoms of the component elements in a simple whole number ratio. However, our knowledge of these atoms is very limited. The only property we know at this point is the relative mass of each atom. Consequently, we cannot answer a wide range of new questions. We need a model which accounts for the periodicity of chemical and physical properties as expressed in the Periodic Table. Why are elements which are very dissimilar in atomic mass nevertheless very similar in properties? Why do these common properties recur periodically?

We would like to understand what determines the number of atoms of each type which combine to form stable compounds. Why are some combinations found and other combinations not observed? Why do some elements with very dissimilar atomic masses (for example, iodine and chlorine) form very similar chemical compounds? Why do other elements with very similar atomic masses (for example, oxygen and nitrogen) form very dissimilar compounds? In general, what forces hold atoms together in forming a molecule?

Answering these questions requires knowledge of the structure of the atom, including how the structures of atoms of different elements are different. Our model should tell us how these structural differences result in the different bonding properties of the different atoms.

Observation 1: Scattering of α particles by atoms

We have assumed that atoms contain positive and negative charges and the number of these charges is equal in any given atom. However, we do not know what that number is, nor do we know how those charges are arranged inside the atom. To determine the location of the charges in the atom, we perform a "scattering" experiment. The idea is straightforward: since we cannot "see" the atomic structure, then we instead "throw" things at the atom and watch the way in which these objects are deflected by the atom. Working backwards, we can then deduce what the structure of the atom must be.

The atoms we choose to shoot at are gold, in the form of a very thin gold foil of thickness about 10^{-4} cm. The objects we "throw" are actually α particles, which are positively charged and fairly massive, emitted by radioactive polonium nuclei. The α particles are directed in a very precise narrow line perpendicular to and in the direction of the gold foil. We then look for α particles at various angles about the gold foil, looking both for particles which have been deflected as they pass through the foil or which have been reflected as they bounce off of the foil. The scattering experiment is illustrated here.

α particle Scattering from Gold Foil

α particles

α source

Gold Foil
0.0001 cm thick
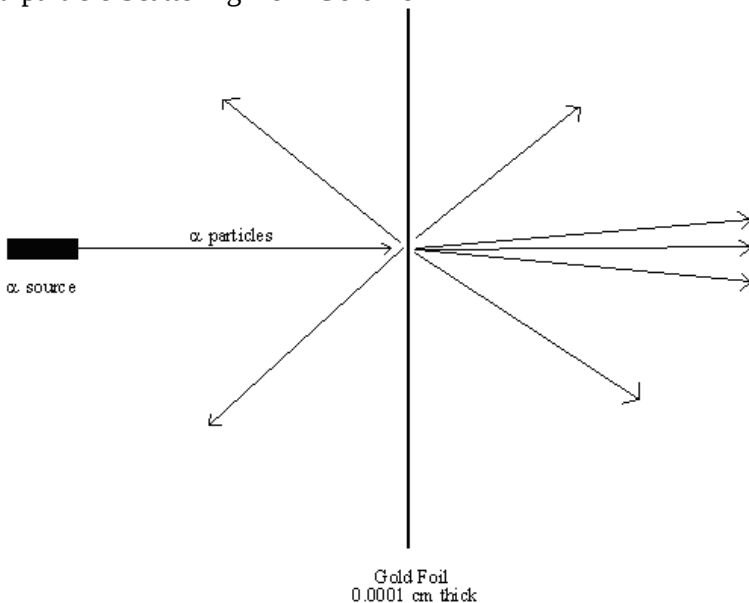
The result of the experiment is initially counter-intuitive. Most of the α particles pass through the gold foil undeflected, as if there had been nothing in their path! A smaller number of the particles are deflected sharply as they pass through the foil, and a very small fraction of the α particles are reflected backwards off of the gold foil. How can we simultaneously account for the lack of any deflection for most of the α particles and for the deflection through large angles of a very small number of particles?

First, since the majority of the positively charged α particles pass through the gold foil undeflected, we can conclude that most of the volume of each gold atom is empty space, containing nothing which might deflect an α particle. Second, since a few of the positively charged α particles are deflected very sharply, then they must encounter a positively charged massive particle inside the atom. We therefore conclude that all of the positive charge and most of the mass of an atom is contained in a **nucleus**. The nucleus must be very small, very massive, and positively charged if it is to account for the sharp deflections. A detailed calculation based assuming this model reveals that the nucleus must be about 100,000 times smaller than the size of the atom itself. The electrons, already known to be contained in the atom, must be outside of the nucleus, since the nucleus is positively charged. They must move in the remaining space of the much larger volume of the atom. Moreover, in total, the electrons comprise less than 0.05% of the total mass of an atom.

This model accounts for observation of both undeflected passage most of α particles and sharp deflection of a few. Most α particles pass through the vast empty space of the atom, which is occupied only by electron. Even the occasional encounter with one of the electrons has no effect on an α particle's path, since each α particle is much more massive than an electron. However, the

nucleus is both massive and positively charged, but it is also small. The rare encounter of an α particle with the nucleus will result in very large deflections; a head-on collision with a gold atom nucleus will send an α particle directly back to its source.

Observation 2: X-ray emission

Although we can now conclude that an atom has a nuclear structure, with positive charge concentrated in a very small nucleus and a number of electrons moving about the nucleus in a much larger volume, we do not have any information on how many electrons there are in an atom of any given element or whether this number depends on the type of atom. Does a gold atom have the same number of electrons as a silver atom? All we can conclude from the data given is that the number of positive charges in the nucleus must exactly equal the number of electrons moving outside the nucleus, since each atom is neutral. Our next difficulty is that we do not know what these numbers are.

The relevant observation seems unrelated to the previous observations. In this case, we examine the frequency of x-rays emitted by atoms which have been energized in an electrical arc. Each type of atom (each element) emits a few characteristic frequencies of x-rays, which differ from one atom to the next. The lowest x-ray frequency emitted by each element is found to increase with increasing position in the periodic table.

Most amazingly, there is an unexpected relationship between the frequency and the relative mass of each atom. Let's rank order the elements by atomic mass, and assign an integer to each according to its ranking in order by mass. In the Periodic Table, this rank order number also corresponds to the element's position in the Periodic Table. For example, Hydrogen is assigned 1, Helium is assigned 2, etc. If we now plot the lowest frequency versus the position number in the periodic table, we find that the frequency increases directly as a simple function of the ranking number. This is shown here, where we have plotted the square root of the x-ray frequency as a function of the ranking number. After a single correction, there is a simple straight-line relationship between these numbers. (The single correction is that the rankings of Argon and Potassium must be reversed. These elements have very similar atomic masses. Although Argon atoms are slightly more massive than Potassium atoms, the Periodic Law requires that we place Argon before Potassium, since Argon is a member of the inert gas group and Potassium is a member of the alkali metal group. By switching their order to correspond to the Periodic Table, we can maintain the beautiful relationship shown here.)
X-ray Frequencies Versus Atomic Number

Atomic Number
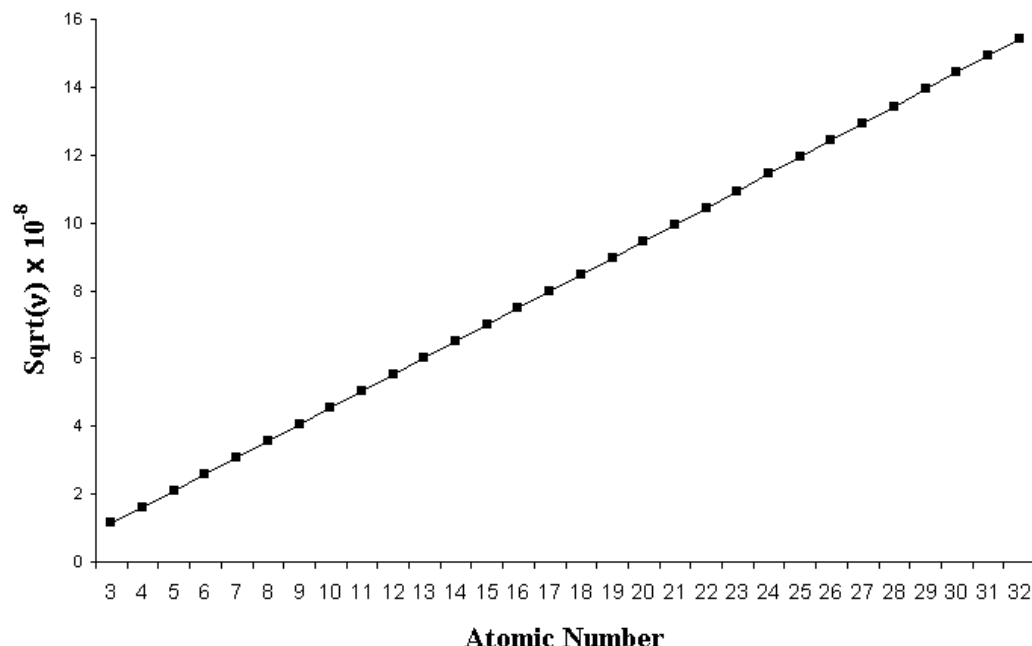
Why is this simple relationship a surprise? The integer ranking of an element by mass would not seem to be a physical property. We simply assigned these numbers in a listing of the elements which we constructed. However, we have discovered that there is a simple quantitative relationship between a real physical quantity (the x-ray frequency) and the ranking number we assigned. Moreover, there are no "breaks" in the straight line shown here, meaning that all of the elements in our mass list must be accounted for. Both observations reveal that the ranking number of each atom must also be a real physical quantity itself, directly related to a structural property of each atom. We now call the ranking number the **atomic number**, since it is a number which uniquely characterizes each atom.

Furthermore, we know that each atom must possess an integer number of positive charges. Since the x-ray data demonstrates a physical property, the atomic number, which is also an integer, the simplest conclusion is that the atomic number from the x-ray data is the number of positive charges in the nucleus. Since each atom is neutral, the atomic number must also equal the number of electrons in a neutral atom.

We now know a great deal about the structure of an atom. We know that the atom has a nuclear structure, we know that the positive charges and mass of the atom are concentrated in the nucleus, and we know how many protons and electrons each atom has. However, we do not yet know anything about the positioning and movement of the electrons in the vast space surrounding the nucleus.

Observation 3: Ionization energies of the atoms

Each electron must move about the nucleus in an electrical field generated by the positive charge of the nucleus and the negative charges of the other electrons. Coulomb's law determines the potential energy of attraction of each electron to the nucleus:
**Equation:**

$$V(r) = \frac{((Z)e)(-e)}{r}$$

where $(Z)e$ is the charge on the nucleus with atomic number Z and $-e$ is the charge on the electron, and r is the distance from the electron to the nucleus. The potential energy of an electron in an atom is negative. This is because we take the potential energy of the electron when removed to great distance from the atom (very large r) to be zero, since the electron and the nucleus do not interact at large distance. In order to remove an electron from an atom, we have to raise the potential energy from its negative value to zero. According to Coulomb's law, we expect electrons closer to the nucleus to have a lower potential energy and thus to require more energy to remove from the atom.

We can directly measure how much energy is required to remove an electron from an atom. Without concerning ourselves with how this measurement is made, we simply measure the minimum amount of energy required to carry out the following "ionization reaction":
Equation:

$$A(\text{g}) \rightarrow A^+(\text{g}) + e^-(\text{g})$$
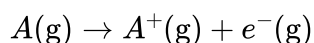
Here, A is an atom in the gas phase, and A^+ is the same atom with one electron e^- removed and is thus an ion. The minimum energy required to perform the ionization is called the **ionization energy**. The values of the ionization energy for each atom in Groups I through VIII of the periodic table are shown as a function of the atomic number here.
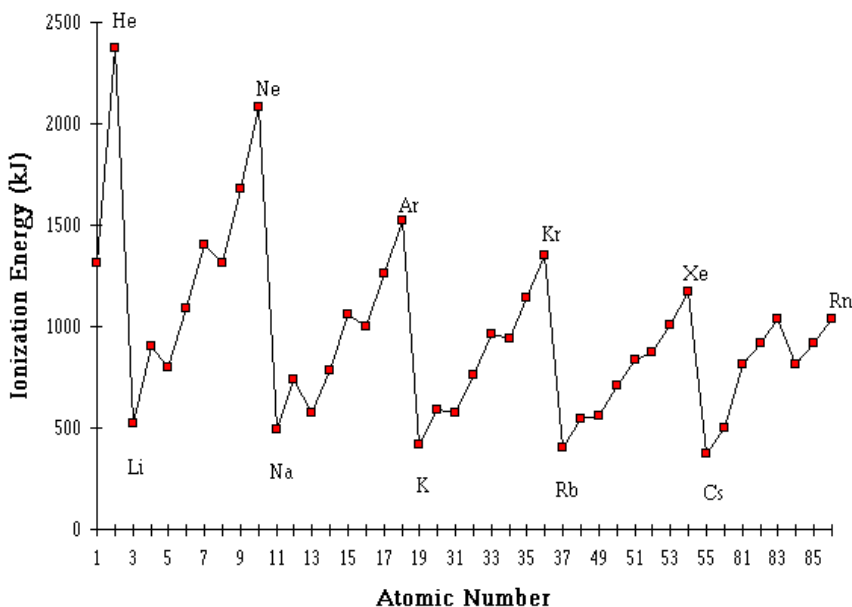
This figure is very reminiscent of the Periodic Law, which states that chemical and physical properties of the elements are periodic functions of the atomic number. Notice that the elements with the largest ionization energies (in other words, the most tightly bound electrons) are the inert gases. By contrast, the alkali metals are the elements with the smallest ionization energies. In a single

period of the periodic table, between each alkali metal atom and the next inert gas atom, the ionization energy rises fairly steadily, falling dramatically from the inert gas to the following alkali metal at the start of the next period.

We need a model which accounts for these variations in the ionization energy. A reasonable assumption from Coulomb's law is that these variations are due to variations in the nuclear charge (atomic number) and in the distance of the electrons from the nucleus. To begin, we can make a very crude approximation that the ionization energy is just the negative of this attractive potential energy given by Coulomb's law. This is crude because we have ignored the kinetic energy and because each electron may not have fixed value of r.

Nevertheless, this approximation gives a way to analyze this figure. For example, from Coulomb's law it seems to make sense that the ionization energy should increase with increasing atomic number. It is easier to remove an electron from Lithium than from Neon because the nuclear charge in Lithium is much smaller than in Neon. But this cannot be the whole picture, because this argument would imply that Sodium atoms should have greater ionization energy than Neon atoms, when in fact Sodium atoms have a very much lower ionization energy. Similarly, although the ionization energy rises as we go from Sodium to Argon, the ionization energy of Argon is still less than that of Neon, even though the nuclear charge in an Argon atom is much greater than the nuclear charge in a Neon atom. What have we omitted from our analysis?

The answer is that we must consider also the distance of the electrons from the nucleus. Since it requires much less energy to ionize a Sodium atom than to ionize a Neon atom even though Sodium's nuclear charge is greater, it must be that the electron which we remove from a Sodium atom is much farther from the nucleus than the electron in the Neon atom. We can make the same comparison of the electrons removed during ionization of Neon and Argon atoms: the Argon electron must be farther from the nucleus than the Neon electron.

On the other hand, since the ionization energy fairly smoothly increases as we move from Lithium to Neon in the second period of elements, this reveals that the electrons are increasingly attracted to the nucleus for greater nuclear charge and suggests that the electrons' distance from the nucleus might not be varying too greatly over the course of a single period of the table.

If we follow this reasoning, we can even estimate how far an electron might typically be from the nucleus by using our crude approximation that the ionization energy is equal to the negative of the Coulomb potential and solving for r for each atom. This gives an estimate of distance of the electron from the nucleus:
Equation:

$$r_{\text{shell}} = -\frac{((Z)e)(-e)}{\text{ionization energy}}$$

Values of r_{shell} calculated in this way are shown for the first 20 elements here. Also shown for comparison is the ionization energy for these elements. Notice that the approximate distance of the electrons from the nucleus increases in steps exactly coinciding with the increases and dips in the ionization energy.
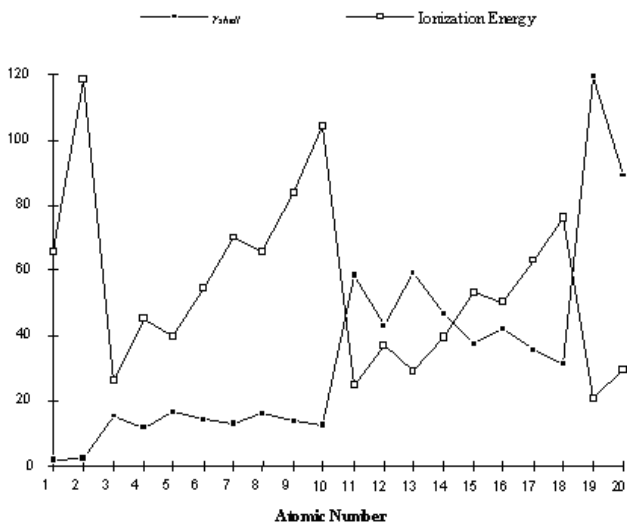
Although these distances we have calculated do not have a precise physical meaning, this figure suggests a significant conclusion. The electrons in the elements are arranged into "shells" of increasingly greater distance from the nucleus. Hydrogen and Helium, with one and two electrons, have ionization energies consistent with electrons at similar and close distance from the nucleus. Then the second row elements lithium through neon have virtually identical sizes, though larger than that for the first two elements. The third row elements, sodium argon, have an approximate electron-nuclear distance which fluctuates a bit but is consistently larger than the second row elements.

Because the sizes of the atoms appear to grow in steps which correspond exactly to the periods of the Periodic Table, it seems that the electrons in the atoms are grouped into sets which are differing distances away from the nucleus. The first two electrons, as in Helium, are close to the nucleus, whereas additional electrons, as in Lithium to Neon, are farther from the nucleus than the first two. The suggests that, for atoms Lithium to Neon, the first two electrons are in an inner "shell", and the remaining electrons are in an outer "shell."

We can refine this shell model for the electrons in an atom with further analysis of ionization energies. We can remove any number of electrons in sequence, forming ions with greater charge. We have been examining the first ionization energy,IE_1, but each successively removed electron has successively greater ionization energy:

First ionization energy IE_1:
Equation:

$$A(g) \rightarrow A^+(g) + e^-(g)$$
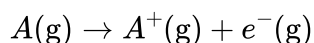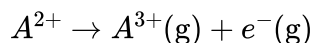
Second ionization energy IE_2:
Equation:

$$A^+(g) \rightarrow A^{2+}(g) + e^-(g)$$
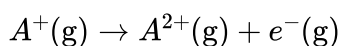
Third ionization energy IE_3:
Equation:

$$A^{2+} \rightarrow A^{3+}(g) + e^-(g)$$

The sequential ionization energies for the elements in the second row of the periodic table are shown here.

	Na	Mg	Al	Si	P	S	Cl	Ar
IE_1	496	738	578	787	1012	1000	1251	1520
IE_2	4562	1451	1817	1577	1903	2251	2297	2665
IE_3	6912	7733	2745	3231	2912	3361	3822	3931
IE_4	9543	10540	11575	4356	4956	4564	5158	5770
IE_5	13353	13630	14830	16091	6273	7013	6542	7238
IE_6	16610	17995	18376	19784	22233	8495	9458	8781
IE_7	20114	21703	23293	23783	25397	27106	11020	11995

Successive Ionization Energies (kJ/mol)

Note that the second ionization energy is always greater than the first, and the third is always greater than the second, etc. This makes sense, since an electron should be more strongly attracted to a positively charged atom than to a neutral atom.

However, the data in the table show a surprising feature. In most cases, the ionization energy increases a fairly large amount for successive ionizations. But for each atom, there is one much larger increase in ionization in the sequence. In Na for example, IE_2 is nearly 10 times greater than IE_1. Similarly, IE_3 is five times greater than IE_2 for Mg, although IE_2 is less than twice IE_1. The data for Na through S all show a single large step in addition to the smaller increases in IE.

Looking closely and counting electrons, we see that this unusually large increase always occurs for the ionization where we have already removed all of the outer shell electrons and are now removing an electron from the inner shell. This occurs uniformly across the second row elements, indicating that our shell model is in fact a very accurate predictor of the higher ionization energies. We can now tell how many electrons there are in the outer shell of each atom: it is equal to the number of electrons since the last inert gas.

We can conclude that an inner shell is "filled" once we have the number of electrons equal to the number in an inert gas atom. The subsequent electrons are added to a new outer shell. This is commonly referred to as the **valence shell** of the atom.

However, we do not know why only a limited number of electrons can reside in each shell. There is no obvious reason at this point why all the electrons in an atom do not reside in the shell closest to the nucleus. Similarly, there is no reason given for why the number of electrons in an inert gas atom exactly fills the outer shell, without room for even a single additional electron. These questions must be addressed further.

Review and Discussion Questions

Exercise:

Problem:

Explain how the scattering of α particles from gold foil reveals that an atom contains a massive, positively charged nucleus whose size is much smaller than that of the atom.

Exercise:

Problem:

Explain the significance of the relationship between the frequency of x-ray emission from each atom and the atomic ranking of that atom in the periodic table.

Exercise:

Problem:

Provide experimental evidence which reveals that the electrons in an atom are grouped into a valence shell and inner shell electrons.

Exercise:

Problem:

State and explain the evidence which reveals that the outer shell of each inert gas atom is full.

Exercise:

Problem:

Why does the ionization energy for each successive ionization increase for every atom? Why is the increase from IE_4 to IE_5 in Si much larger than any of the other increases for Si?

Quantum Energy Levels In Atoms

Foundation

The atomic molecular theory provides us a particulate understanding of matter. Each element is characterized as consisting of identical, indestructible atoms with atomic weights which have been determined. Compounds consist of identical molecules, each made up from a specific number of atoms of each of the component elements. We also know that atoms have a nuclear structure, meaning that all of the positive charge and virtually all of the mass of the atom are concentrated in a nucleus which is a very small fraction of the volume of the atom. Finally, we know that the electrons in the atom are arranged in "shells" about the nucleus, with each shell farther from the nucleus that the previous. The electrons in outer shells are more weakly attached to the atom than the electrons in the inner shells, and only a limited number of electrons can fit in each shell.

Goals

The shell model of the atom is a good start in understanding the differences in the chemical properties of the atoms of different elements. For example, we can understand the periodicity of chemical and physical properties from our model, since elements in the same group have the same number of electrons in the valence shell.

However, there are many details missing from our description. Other than a very crude calculation of "distance" of the shells from the nucleus, we have no description of what the differences are between the electrons in different shells. What precisely is a "shell?"

Most importantly, the arrangement of elements into groups and the periodicity of chemical properties both depend on the concept that a shell is "filled" by a certain number of electrons. Looking at the number of elements in each period, the number of electrons which fills a shell depends on which shell is being filled. In some cases, a shell is filled by eight electrons, in others, it appears to be 18 electrons. What determines how many electrons can "fit" in a shell? Why is there a limit at all?

Finally, a closer look at the ionization energies [here](#) reveals that our shell model must be incomplete. Our model implies that the elements of the second period from Lithium to Neon have their valence electrons in the second shell. With increasing nuclear charge, the ionization energy of these atoms should increase from Lithium to Neon. As a general trend, this is true, but there are variations. Note that the ionization energy of Oxygen atoms is less than that of Nitrogen atoms. We need to pursue additional detail in our model of the structure of the atom.

Observation 1: The Spectrum of Hydrogen

To begin, we need to know a little about light. All forms of electromagnetic radiation travel as an oscillating wave, with an electric field component perpendicular to a magnetic field component. As a wave, the radiation can be characterized by its "wavelength", symbolized as λ, which is the distance between adjacent peaks in the wave. Different wavelengths correspond to different forms of electromagnetic radiation. For example, microwave radiation has wavelength in the range of 10^{-2} to 10^{-3} meters, whereas x-ray radiation has wavelength in the range 10^{-9} to 10^{-10} meters. Radiation which is visible to the human eye has wavelength in the very narrow range from 3.8×10^{-7} to 7.8×10^{-7} meters.

Radiation can also be characterized by the frequency of the electromagnetic wave, which is the number of peaks in the wave which pass a point in space per second. Frequency is symbolized by ν. The speed which light travels in a vacuum in the same for all forms of electromagnetic radiation, $c = 2.997 \times 10^8 \frac{m}{s}$. As such, we can relate the frequency of light to the wavelength of light by the equation
Equation:

$$\lambda\left(m\right) \times \nu\left(s^{-1}\right) = c\left(\frac{m}{s}\right)$$

The longer the wavelength λ, the lower the frequency ν. This makes sense when we remember that light travels at a fixed speed. When the wavelength is longer, fewer peaks will pass a point in space in a second. From this

equation, there is a specific relationship between frequency and wavelength, and either or both can be used to characterize the properties of radiation.

With this background in hand, we can use our understanding of light to pursue more data about the energies of electrons in atoms. Ionization energies tell us how much energy is required to remove an electron from an atom, but do not tell what happens if an electron changes its energy in an atom. To analyze this, we need a means to measure the energies gained or lost by an atom. One way to do so is to analyze the "spectrum" of an atom, which is the set of frequencies of light emitted by the atom. Since hydrogen is the simplest atom, we analyze the hydrogen spectrum first. We find that, if we pass a current of electricity through a sample of hydrogen gas, light is emitted. Careful analysis shows that, although some of this light is emitted by H_2 molecules, some of the light is also emitted by H atoms. Since light is a form of energy, then these H atoms must release energy supplied to them by the electrons in the current.

Most importantly, if we pass the light emitted by the hydrogen gas sample through a prism, we can separate the colors as in a rainbow, each with a characteristic frequency. The resultant image of separated colors is called the **spectrum** of hydrogen. We find in this experiment that there are only four frequencies (four colors) of light in the emission that are visible. The most intense of the lines in the spectrum is bright red, but there are blue and violet lines. It turns out that there are also many other frequencies of light emitted which are invisible to the human eye.

Careful observation and analysis reveals that every frequency in the hydrogen atom spectrum can be predicted by a very simple formula, called the Rydberg equation:
Equation:

$$\nu = R \times \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

where R is the Rydberg constant ($3.29 \times 10^{15} s^{-1}$). n and m are integers (1,2,3,...). Each choice of n and m predicts a single observed frequency in the hydrogen atom spectrum.

The atoms of all elements emit radiation when energized in an electric current, and as do all molecules of all compounds. However, we find that the specific frequencies of light emitted are characteristic of each atom or molecule. In other words, the spectrum of each element is unique to each element or compound. As a result, the spectrum of each substance can be used to identify that substance. (Note that the Rydberg equation tells us only the spectrum of hydrogen.)

Our interest is in the fact that the radiation emitted by an atom tells us about the amounts of energy which can be released by an atom. For a hydrogen atom, for example, these changes in energy must correspond to the amounts of energy which the electrons inside the atom can gain or lose.

At this point, we need to relate the frequency of radiation emitted by an atom to the amount of energy lost by the electron in the atom. We thus examine some observations about the energy of radiation.

Observation 2: The Photoelectric Effect

When a light source is directed at a metal surface, it is found under many circumstances that electrons are ejected from the surface. This phenomenon is called the "photoelectric effect." These electrons can be collected to produce a usable electric current. (This effect has a variety of common practical applications, for example, in "electric eye" devices.) It is reasonable to expect that a certain amount of energy is required to liberate an electron from a metal surface, since the electron is attracted to the positively charged nuclei in the metal. Thus, in order for the electron to escape, the light must supply sufficient energy to the electron to overcome this attraction.

The following experimental observations are found when studying the photoelectric effect. First, in order for the effect to be observed, the light must be of at least a minimum frequency which we call the **threshold frequency**, ν_0. This frequency is a characteristic for a given metal. That is, it is the same value for each sample of that metal, but it varies from one metal to the next. For low frequency light, photoelectrons are not observed in any number, no matter how intense the light source is. For light with

frequency above ν_0, the number of photoelectrons emitted by the metal (measured by the photoelectric current, Φ) increases directly with the intensity of the light. These results are shown in [link].

The Photoelectric Effect

For photoelectrons to be emitted, the light frequency must be greater than a threshold value.

If the frequency is high enough, the number of photoelectrons increases directly with the light intensity.
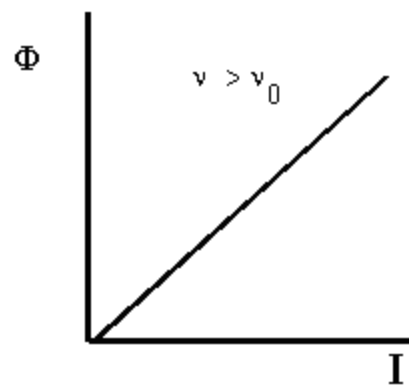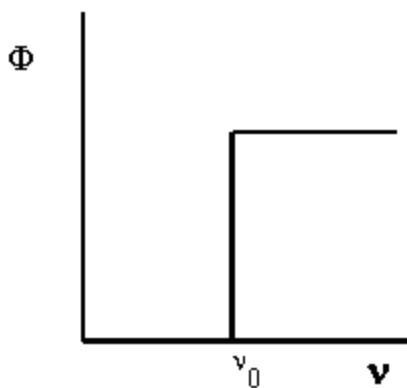
Φ is the photoelectric current, ν is the frequency of incident light, and I is the intensity of incident light.

Second, we can measure the energies of the electrons emitted by the metal. For a given metal, all photoelectrons have the same kinetic energy for a fixed frequency of light above ν_0. This fixed kinetic energy is independent of the intensity of the light source. As the frequency of the light is increased, the kinetic energy of the emitted electrons increases proportionally. These results are shown in [link].

More Photoelectric Effect

If the frequency is high enough, the energy of the electrons increases directly with the frequency.

However, the energy of the photolectrons does not depend on the light intensity.
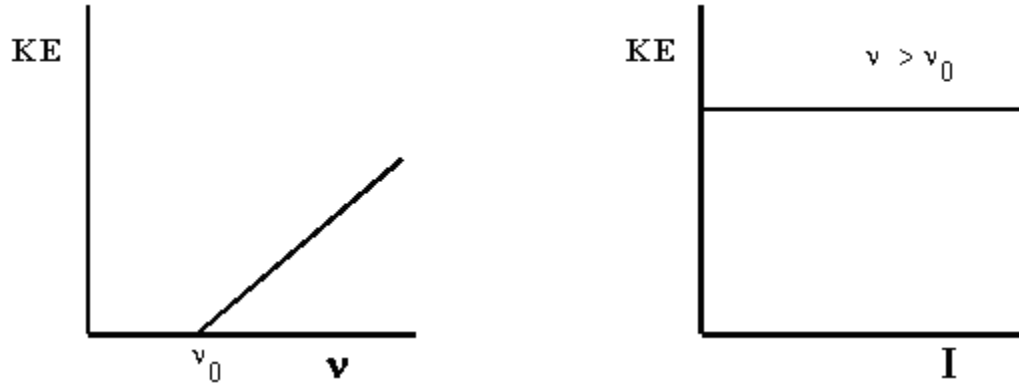
KE is the photoelectron kinetic energy, ν is the frequency of incident light, and I is the intensity of incident light.

Are these results surprising? To the physicists at the end of the nineteenth century, the answer was yes, very surprising indeed. They expected that the energy of the light source should be determined by its intensity. Hence, the energy required to eject a photoelectron should be supplied by light of high intensity, no matter how low the frequency of the radiation. Thus, there should be no threshold frequency, below which no electrons are emitted. Moreover, the kinetic energy of the electrons should increase with intensity, not with light frequency. These predictions are not observed, so the results are counter to physical intuition.

We can account for these results in a straightforward but perhaps non-obvious manner. (Einstein provided the explanation in 1905.) Since the kinetic energy of the emitted photoelectrons increases proportionally with increases in the frequency of the light above the threshold frequency, we can conclude from conservation of total energy that the energy supplied by the light to the ejected electron must be proportional to its frequency: $E \propto \nu$. This does not immediately account for the existence of the threshold frequency, though, since it would still seem to be the case that even low frequency light would possess high energy if the intensity were sufficient. By this reasoning, high intensity, low frequency light should

therefore produce as many photoelectrons as are produced by low intensity, high frequency light. But this is not observed.

This is a very challenging puzzle, and an analogy helps to reveal the subtle answer. Imagine trying to knock pieces out of a wall by throwing objects at it. We discover that, no matter how many ping pong balls we throw, we cannot knock out a piece of the wall. On the other hand, only a single bowling ball is required to accomplish the task. The results of this "experiment" are similar to the observations of the photoelectric effect: very little high frequency light can accomplish what an enormous amount of low frequency light cannot. The key to understanding our imaginary experiment is knowing that, although there are many more ping-pong balls than bowling balls, it is only the impact of each individual particle with the wall which determines what happens.

Reasoning from this analogy, we must conclude that the energy of the light is supplied in "bundles" or "packets" of constant energy, which we will call **photons**. We have already concluded that the light supplies energy to the electron which is proportional to the light frequency. Now we can say that the energy of each photon is proportional to the frequency of the light. The intensity of the light is proportional to the number of these packets. This now accounts for the threshold frequency in a straightforward way. For a photon to dislodge a photoelectron, it must have sufficient energy, by itself, to supply to the electron to overcome its attraction to the metal. Although increasing the intensity of the light does increase the total energy of the light, it does not increase the energy of an individual photon. Therefore, if the frequency of the light is too low, the photon energy is too low to eject an electron. Referring back to the analogy, we can say that a single bowling bowl can accomplish what many ping-pong balls cannot, and a single high frequency photon can accomplish what many low frequency photons cannot.

The important conclusion for our purposes is that **light energy is quantized into packets of energy**. The amount of energy in each photon is given by Einstein's equation,
Equation:

$$E = h\nu$$

where h is a constant called Planck's constant.

Quantized Energy Levels in Hydrogen Atoms

We can combine the observation of the hydrogen atom spectrum with our deduction that light energy is quantized into packets to reach an important conclusion. Each frequency of light in the spectrum corresponds to a particular energy of light and, therefore, to a particular energy **loss** by a hydrogen atom, since this light energy is quantized into packets. Furthermore, since only certain frequencies are observed, then only certain energy losses are possible. This is only reasonable if the energy of each hydrogen atom is restricted to certain specific values. If the hydrogen atom could possess any energy, then it could lose any amount of energy and emit a photon of any energy and frequency. But this is not observed. Therefore, the energy of the electron in a hydrogen atom must be restricted to certain **energy levels**.

The Hydrogen atom spectrum also tells us what these energy levels are. Recall that the frequencies of radiation emitted by Hydrogen atoms are given by the [Rydberg equation](). Each choice of the positive integers n and m predicts a single observed frequency in the hydrogen atom spectrum.

Each emitted frequency must correspond to an energy $h\nu$ by [Einstein's equation](). This photon energy must be the **difference** between two energy levels for a hydrogen electron, since that is the amount of energy released by the electron moving from one level to the other. If the energies of the two levels are E_m and E_n, then we can write that
Equation:

$$h\nu = E_m - E_n$$

By comparing this to the Rydberg equation, each energy level must be given by the formula
Equation:

$$E_n = (-h)R\frac{1}{n^2}$$

We can draw two conclusions. First, the electron in a hydrogen atom can exist only with certain energies, corresponding to motion in what we now call a state or an **orbital**. Second, the energy of a state can be characterized by an integer **quantum number**, n = 1, 2, 3, ... which determines its energy.

These conclusions are reinforced by similar observations of spectra produced by passing a current through other elements. Only specific frequencies are observed for each atom, although only the hydrogen frequencies obey the Rydberg formula.

We conclude that the energies of electrons in atoms are "quantized," that is, restricted to certain values. We now need to relate this quantization of energy to the existence of shells, as developed in a previous study.

Observation 3: Photoelectron Spectroscopy of Multi-Electron Atoms

The ionization energy of an atom tells us the energy of the electron or electrons which are at highest energy in the atom and are thus easiest to remove from the atom. To further analyze the energies of the electrons more tightly bound to the nucleus, we introduce a new experiment. The photoelectric effect can be applied to ionize atoms in a gas, in a process often called **photoionization**. We shine light on an atom and measure the minimum frequency of light, corresponding to a minimum energy, which will ionize an electron from an atom. When the frequency of light is too low, the photons in that light do not have enough energy to ionize electrons from an atom. As we increase the frequency of the light, we find a threshold at which electrons begin to ionize. Above this threshold, the energy $h\nu$ of the light of frequency ν is greater than the energy required to ionize the atom, and the excess energy is retained by the ionized electron as kinetic energy.

In photoelectron spectroscopy, we measure the kinetic energy of the electrons which are ionized by light. This provides a means of measuring the ionization energy of the electrons. By conservation of energy, the energy of the light is equal to the ionization energy IE plus the kinetic energy KE of the ionized electron:

Equation:

$$h\nu = \mathrm{IE} + \mathrm{KE}$$

Thus, if we use a known frequency ν and measure KE, we can determine IE. The more tightly bound an electron is to the atom, the higher the ionization energy and the smaller the kinetic energy of the ionized electron. If an atom has more than one electron and these electrons have different energies, then for a given frequency of light, we can expect electrons to be ejected with different kinetic energies. The higher kinetic energies correspond to the weakly bound outer electrons, and the lower kinetic energies correspond to the tightly bound inner electrons.

The ionization energies for the first twenty elements are given in [link]. We note that there is a single ionization energy for hydrogen and helium. This is consistent with the shell model of these atoms since, in both of these atoms, the electron or electrons are in the innermost shell. The energies of these electrons correspond to the $n = 1$ energy level of the hydrogen atom. In lithium and beryllium, there are two ionization energies. Again, this is consistent with the shell model, since now there are electrons in both of the first two shells. Note also that the ionization energy of the inner shell electrons increases as we go from hydrogen to lithium to beryllium, because of the increase in nuclear charge. The lower energy electrons correspond to the $n = 1$ energy level of hydrogen and the higher energy electrons correspond to the $n = 2$ energy level.

Element	Ionization Energy (MJ/mol)

Element	Ionization Energy (MJ/mol)					
H	1.31					
He	2.37					
Li	6.26	0.52				
Be	11.5	0.90				
B	19.3	1.36	0.80			
C	28.6	1.72	1.09			
N	39.6	2.45	1.40			
O	52.6	3.12	1.31			
F	67.2	3.88	1.68			
Ne	84.0	4.68	2.08			
Na	104	6.84	3.67	0.50		
Mg	126	9.07	5.31	0.74		
Al	151	12.1	7.79	1.09	0.58	
Si	178	15.1	10.3	1.46	0.79	
P	208	18.7	13.5	1.95	1.01	
S	239	22.7	16.5	2.05	1.00	
Cl	273	26.8	20.2	2.44	1.25	

Element	Ionization Energy (MJ/mol)					
Ar	309	31.5	24.1	2.82	1.52	
K	347	37.1	29.1	3.93	2.38	0.42
Ca	390	42.7	34.0	4.65	2.9	0.59

Surprisingly, though, boron has three ionization energies, which does not seem consistent with the shell model. From the hydrogen atom energy levels, we would have expected that all $n = 2$ electrons would have the same energy. We can note that the two smaller ionization energies in boron are comparable in magnitude and smaller by more than a factor of ten than the ionization energy of the electrons in the inner shell. Thus, the electrons in the outer $n = 2$ shell apparently have comparable energies, but they are not identical. The separation of the second shell into two groups of electrons with two comparable but different energies is apparent for elements boron to neon.

As such, we conclude from the experimental data that the second shell of electrons should be described as two **subshells** with slightly different energies. For historical reasons, these subshells are referred to as the as the "2s" and "2p" subshells, with 2s electrons slightly lower in energy than 2p electrons. The energies of the 2s and 2p electrons decrease from boron to neon, consistent with the increase in the nuclear charge.

Beginning with sodium, we observe four distinct ionization energies, and beginning with aluminum there are five. Note for these elements that the fourth and fifth ionization energies are again roughly a factor of ten smaller than the second and third ionization energies, which are in turn at least a factor of ten less than the first ionization energy. Thus, it appears that there are three shells of electrons for these atoms, consistent with our previous shell model. As with $n = 2$, the $n = 3$ shell is again divided into two subshells, now called the 3s and 3p subshells.

These data also reveal how many electrons can reside in each subshell. In each n level, there are two elements which have only the ionization energy

for the s subshell. Hence, s subshells can hold two electrons. By contrast, there are 6 elements which have both the s and p subshell ionization energies, so the p subshell can hold 6 electrons.

The shell and subshell organization of electron energies can also be observed by measuring the "electron affinity" of the atoms. Electron affinity is the energy released when an electron is added to an atom:
Equation:

$$A(g) + e^-(g) \rightarrow A^-(g)$$
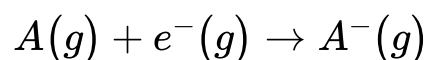
If there is a strong attraction between the atom A and the added electron, then a large amount of energy is released during this reaction, and the electron affinity is a large positive number. (As a note, this convention is the opposite of the one usually applied for energy changes in reactions: exothermic reactions, which give off energy, conventionally have negative energy changes.)

The electron affinities of the halogens are large positive values: the electron affinities of F, Cl, and Br are 328.0 kJ/mol, 348.8 kJ/mol, and 324.6 kJ/mol. Thus, the attached electrons are strongly attracted to the nucleus in each of these atoms. This is because there is room in the current subshell to add an additional electron, since each atom has 5 p electrons, and the core charge felt by the electron in that subshell is large.

By contrast, the electron affinities of the inert gases are **negative**: the addition of an electron to an inert gas atom actually requires the **input** of energy, in effect, to force the electron into place. This is because the added electron cannot fit in the current subshell and must be added to a new shell, farther from the nucleus. As such, the core charge felt by the added electron is very close to zero.

Similarly, the electron affinities of the elements Be, Mg, and Ca are all negative. This is again because the s subshell in these atoms already has two electrons, so the added electron must go into a higher energy subshell with a much smaller core charge.

Electron Waves, the Uncertainty Principle, and Electron Energies

We now have a fairly detailed description of the energies of the electrons in atoms. What we do not have is a model which tells us what factors determine the energy of an electron in a shell or subshell. Nor do we have a model to explain why these energies are similar but different for electrons in different subshells.

A complete answer to these questions requires a development of the quantum theory of electron motion in atoms. Because the postulates of this quantum theory cannot be readily developed from experimental observations, we will concern ourselves with a few important conclusions only.

The first important conclusion is that the motion of an electron in an atom is described by a wave function. Interpretation of the wave motion of electrons is a very complicated proposition, and we will only deal at present with a single important consequence, namely the **uncertainty principle**. A characteristic of wave motion is that, unlike a particle, the wave does not have a definite position at a single point in space. By contrast, the location of a particle is precise. Therefore, since an electron travels as a wave, we must conclude that we cannot determine the precise location of the electron in an atom. This is, for our purposes, the uncertainty principle of quantum mechanics. We **can** make measurements of the location of the electron, but we find that each measurement results in a different value. We are then forced to accept that we cannot determine the precise location. We are allowed, however, to determine a **probability distribution** for where the electron is observed.

This probability distribution is determined by quantum mechanics. The motion of the electron in a hydrogen atom is described by a function, often called the **wave function** or the **electron orbital** and typically designated by the symbol Ψ. Ψ is a function of the position of the electron $\boldsymbol{r}$, and quantum mechanics tells us that $\left(|\Psi|\right)^2$ is the **probability** of observing the electron at the location $\boldsymbol{r}$.

Each electron orbital has an associated constant value of the electronic energy, E_n, in agreement with our earlier conclusions. In fact, quantum mechanics exactly predicts the energy shells and the hydrogen atom spectrum we observe. The energy of an electron in an orbital is determined primarily by two characteristics of the orbital. The first, rather intuitive, property determines the average potential energy of the electron: an orbital which has substantial probability in regions of low potential energy will have a low total energy. By Coulomb's law, the potential energy arising from nucleus-electron attraction is lower when the electron is nearer the nucleus. In atoms with more than one electron, electron-electron repulsion also contributes to the potential energy, as Coulomb's law predicts an increase in potential energy arising from the repulsion of like charges.

A second orbital characteristic determines the contribution of kinetic energy, via a more subtle effect arising out of quantum mechanics. As a consequence of the uncertainty principle, quantum mechanics predicts that, the more confined an electron is to a smaller region of space, the higher must be its average kinetic energy. Since we cannot measure the position of electron precisely, we define the uncertainty in the measurement as $\Delta(x)$. Quantum mechanics also tells us that we cannot measure the momentum of an electron precisely either, so there is an uncertainty $\Delta(p)$ in the momentum. In mathematical detail, the uncertainty principle states that these uncertainties are related by an inequality:
Equation:

$$\Delta(x)\Delta(p) \geq \frac{h}{4\pi}$$

where h is Planck's constant, $6.62 \times 10^{-34}\ (Js)$ (previously seen in [Einstein's equation](#) for the energy of a photon). This inequality reveals that, when an electron moves in a small area with a correspondingly small uncertainty $\Delta(x)$, the uncertainty in the momentum $\Delta(p)$ must be large. For $\Delta(p)$ to be large, the momentum must also be large, and so must be the kinetic energy.

Therefore, the more compact an orbital is, the higher will be the average kinetic energy of an electron in that orbital. This extra kinetic energy, which can be regarded as the **confinement energy**, is comparable in magnitude to the average potential energy of electron-nuclear attraction. Therefore, in general, an electron orbital provides a compromise, somewhat localizing the electron in regions of low potential energy but somewhat delocalizing it to lower its confinement energy.

Electron Orbitals and Subshell Energies

We need to account for the differences in energies of the electrons in different subshells, since we know that, in a Hydrogen atom, the orbital energy depends only on the n quantum number. We recall that, in the Hydrogen atom, there is a **single** electron. The energy of that electron is thus entirely due to its kinetic energy and its attraction to the nucleus. The situation is different in all atoms containing more than one electron, because the energy of the electrons is affected by their mutual repulsion. This repulsion is very difficult to quantify, but our model must take it into account.

A simple way to deal with the effect of electron-electron repulsion is to examine the shell structure of the atom. The two $n = 1$ electrons in beryllium are in a shell with a comparatively short average distance from the nucleus. Therefore, the two $n = 2$ electrons are in a shell which is, on average, "outside" of the $n = 1$ shell. The $n = 1$ electrons are thus the "core" and the $n = 2$ electrons are in the valence shell. This structure allows us to see in a simple way the effect of electron-electron repulsion on the energies of the $n = 2$ electrons. Each $n = 2$ electron is attracted by the +4 charge on the tiny beryllium nucleus, but is repelled by the two -1 charges from the inner shell formed by the two $n = 1$ electrons. Net, then, an $n = 2$ electron effectively "sees" roughly a +2 nuclear charge. We refer to this +2 as the "core charge" since it is the net charge on the core resulting from the balance of attraction to the nucleus and repulsion from the core electrons. The nucleus is partially "shielded" from the valence electrons by the core electrons.

This shielding effect does not seem to account for the difference in ionization energies between 2s and 2p or for the lower ionization energy of boron compared to beryllium, since, in each atom, the valence electrons are in the $n = 2$ shell. However, the shielding effect is not perfect. Recall that we only know the **probabilities** for observing the positions of the electrons. Therefore, we cannot definitely state that the $n = 2$ electrons are outside of the $n = 1$ core. In fact, there is some probability that an $n = 2$ electron might be found inside the $n = 1$ core, an effect called "core penetration." When an $n = 2$ electron does penetrate the core, it is no longer shielded from the nucleus. In this case, the $n = 2$ electron is very strongly attracted to the nucleus and its energy is thus lowered. What is the extent of this penetration? We must consult quantum theory. The answer is in [link], which shows the probability of finding an electron a distance r away from the nucleus for each of the 1s, 2s, and 2p orbitals. We can see that there is a greater probability (though small) for the 2s electron to penetrate the core than for the 2p electron to do so.

Probability for an Electron at a Distance r from a Hydrogen Nucleus
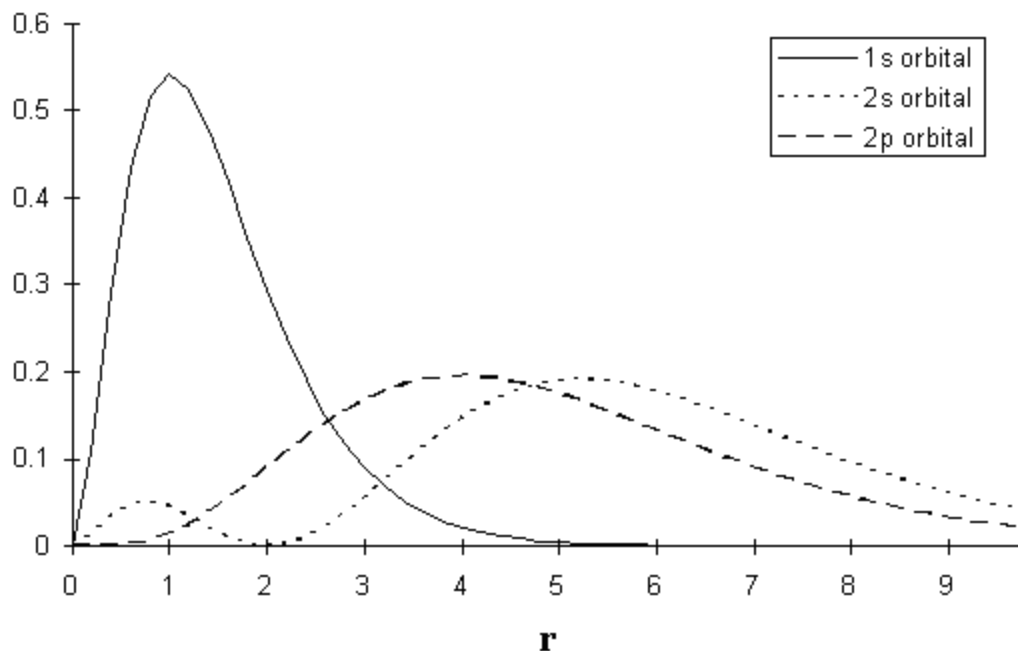
As a result of the core penetration, an electron in a 2s orbital feels a greater "effective nuclear charge" than just the core charge, which was approximated by assuming perfect shielding. Thus the effective nuclear charge for a 2s electron is greater than the effective nuclear charge for a 2p

electron. Therefore, the energy of an electron in the 2s orbital in beryllium is lower than it would be in the 2p orbital.

A detailed analysis from quantum mechanics gives the following ordering of orbitals in order of increasing energy:
Equation:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < ...$$

This ordering can be rationalized on the basis of effective nuclear charge, shielding, and core penetration.

Review and Discussion Questions

Exercise:

  Problem:

  The photoelectric effect demonstrates that radiation energy is quantized into "packets" or photons. Explain how and why this observation is of significance in understanding the structure of atoms.

Exercise:

  Problem:

  Explain how we can know that higher frequency light contains higher energy photons.

Exercise:

  Problem:

  Electron affinity is the energy released when an electron is attached to an atom. If an atom has a positive electron affinity, the added electron is attracted to the nucleus to form a stable negative ion. Why doesn't a Beryllium atom have a positive electron affinity? Explain how this demonstrates that the energy of a 2s orbital is less than the energy of a 2p orbital.

Exercise:

Problem:

Why does an inert gas atom have a high ionization energy but a low electron affinity? Why do these properties combine to make the atoms of inert gases unreactive?

Exercise:

Problem:

Consider electrons from two different subshells in the same atom. In photoelectron spectroscopy, the lower energy electron has a higher ionization energy but is observed to have lower kinetic energy after ionization. Reconcile the lower energy with the higher ionization energy with the lower kinetic energy.

Exercise:

Problem:

Chlorine atoms have 5 distinct ionization energies. Explain why. Predict the number of ionization energies for Bromine atoms, and explain your answer. (Hint: examine the structure of the periodic table.)

Exercise:

Problem:

Why does a Bromine atom have a much smaller radius than a Potassium atom, even though a Br atom has 16 more electrons than does a K atom?

Exercise:

Problem:

Explain why electrons confined to smaller orbitals are expected to have higher kinetic energies.

Exercise:

Problem:

Define "shielding" in the context of electron-electron repulsion. What is the significance of shielding in determining the energy of an electron? How is the affected by core penetration?

Covalent Bonding and Electron Pair Sharing

Foundation

We begin with our understanding of the relationship between chemical behavior and atomic structure. That is, we assume the Periodic Law that the chemical and physical properties of the elements are periodic functions of atomic number. We further assume the structure of the atom as a massive, positively charged nucleus, whose size is much smaller than that of the atom as a whole, surrounded by a vast open space in which move negatively charged electrons. These electrons can be effectively partitioned into a core and a valence shell, and it is only the electrons in the valence shell which are significant to the chemical properties of the atom. The number of valence electrons in each atom is equal to the group number of that element in the Periodic Table.

Goals

The atomic molecular theory is extremely useful in explaining what it means to form a compound its component elements. That is, a compound consists of identical molecules, each comprised of the atoms of the component elements in a simple whole number ratio. However, the atomic molecular theory also opens up a wide range of new questions. We would like to know what atomic properties determine the number of atoms of each type which combine to form stable compounds. Why are some combinations observed and other combinations not observed? Some elements with very dissimilar atomic masses (for example, iodine and chlorine) form very similar chemical compounds, but other elements with very similar atomic masses (for example, oxygen and nitrogen) form very dissimilar compounds. What factors are responsible for the bonding properties of the elements in a similar group? In general, we need to know what forces hold atoms together in forming a molecule.

We have developed a detail understanding of the structure of the atom. Our task now is to apply this understanding to develop a similar level of detail about how atoms bond together to form molecules.

Observation 1: Valence and the Periodic Table

To begin our analysis of chemical bonding, we define the **valence** of an atom by its tendencies to form molecules. The inert gases do not tend to combine with any other atoms. We thus assign their valence as 0, meaning that these atoms tend to form 0 bonds. Each halogen prefers to form molecules by combining with a single hydrogen atom (e.g. HF, H Cl). We thus assign their valence as 1, also taking hydrogen to also have a valence of 1. What we mean by a valence of 1 is that these atoms prefer to bind to only one other atom. The valence of oxygen, sulfur, etc. is assigned as 2, since two hydrogens are required to satisfy bonding needs of these atoms. Nitrogen, phosphorus, etc. have a valence of 3, and carbon and silicon have a valence of 4. This concept also applies to elements just following the inert gases. Lithium, sodium, potassium, and rubidium bind with a single halogen atom. Therefore, they also have a valence of 1. Correspondingly, it is not surprising to find that, for example, the combination of two potassium atoms with a single oxygen atom forms a stable molecule, since oxygen's valence of 2 is be satisfied by the two alkali atoms, each with valence 1. We can proceed in this manner to assign a valence to each element, by simply determining the number of atoms to which this element's atoms prefer to bind.

In doing so, we discover that the periodic table is a representation of the valences of the elements: elements in the same group all share a common valence. The inert gases with a valence of 0 sit to one side of the table. Each inert gas is immediately preceded in the table by one of the halogens: fluorine precedes neon, chlorine precedes argon, bromine precedes krypton, and iodine precedes xenon. And each halogen has a valence of one. This "one step away, valence of one" pattern can be extended. The elements just prior to the halogens (oxygen, sulfur, selenium, tellurium) are each two steps away from the inert gases in the table, and each of these elements has a valence of two (e.g. H_2O, H_2S). The elements just preceding these (nitrogen, phosphorus, antimony, arsenic) have valences of three (e.g. NH_3, PH_3), and the elements before that (carbon and silicon most notably) have valences of four (CH_4, Si H_4). The two groups of elements immediately after the inert gases, the alkali metals and the alkaline earths, have valences of one and two, respectively. Hence, for many elements in the periodic

table, the valence of its atoms can be predicted from the number of steps the element is away from the nearest inert gas in the table. This systemization is quite remarkable and is very useful for remembering what molecules may be easily formed by a particular element.

Next we discover that there is a pattern to the valences: for elements in groups 4 through 8 (e.g. carbon through neon), the valence of each atom **plus** the number of electrons in the valence shell in that atom always equals **eight**. For examples, carbon has a valence of 4 and has 4 valence electrons, nitrogen has a valence of 3 and has 5 valence electrons, and oxygen has a valence of 2 and has 6 valence electrons. Hydrogen is an important special case with a single valence electron and a valence of 1. Interestingly, for each of these atoms, the number of bonds the atom forms is equal to the number of vacancies in its valence shell.

To account for this pattern, we develop a model assuming that each atom attempts to bond to other atoms so as to completely fill its valence shell with electrons. For elements in groups 4 through 8, this means that each atom attempts to complete an "octet" of valence shell electrons. (Why atoms should behave this way is a question unanswered by this model.) Consider, for example, the combination of hydrogen and chlorine to form hydrogen chloride, $H\text{Cl}$. The chlorine atom has seven valence electrons and seeks to add a single electron to complete an octet. Hence, chlorine has a valence of 1. Either hydrogen or chlorine could satisfy its valence by "taking" an electron from the other atom, but this would leave the second atom now needing two electrons to complete its valence shell. The only way for both atoms to complete their valence shells simultaneously is to **share** two electrons. Each atom donates a single electron to the electron pair which is shared. It is this sharing of electrons that we refer to as a chemical bond, or more specifically, as a **covalent bond**, so named because the bond acts to satisfy the valence of both atoms. The two atoms are thus held together by the need to share the electron pair.

Observation 2: Compounds of Carbon and Hydrogen

Many of the most important chemical fuels are compounds composed entirely of carbon and hydrogen, i.e. hydrocarbons. The smallest of these is

methane CH_4, a primary component of household natural gas. Other simple common fuels include ethane C_2H_6, propane C_3H_8, butane C_4H_{10}, pentane C_5H_{12}, hexane C_6H_{14}, heptane C_7H_{16}, and octane C_8H_{18}. It is interesting to note that there is a consistency in these molecular formulae: in each case, the number of hydrogen atoms is two more than twice the number of carbon atoms, so that each compound has a molecular formula like C_nH_{2n+2}. This suggests that there are strong similarities in the valences of the atoms involved which should be understandable in terms of our valence shell electron pair sharing model. In each molecule, the carbon atoms must be directly bonded together, since they cannot be joined together with a hydrogen atom. In the easiest example of ethane, the two carbon atoms are bonded together, and each carbon atom is in turn bonded to three hydrogen atoms. Thus, in this case, it is relatively apparent that the valence of each carbon atom is 4, just as in methane, since each is bonded to four other atoms. Therefore, by sharing an electron pair with each of the four atoms to which it is bonded, each carbon atom has a valence shell of eight electrons.

In most other cases, it is not so trivial to determine which atoms are bonded to which, as there may be multiple possibilities which satisfy all atomic valences. Nor is it trivial, as the number of atoms and electrons increases, to determine whether each atom has an octet of electrons in its valence shell. We need a system of electron accounting which permits us to see these features more clearly. To this end, we adopt a standard notation for each atom which displays the number of valence electrons in the unbonded atom explicitly. In this notation, carbon and hydrogen look like [link], representing the single valence electron in hydrogen and the four valence electrons in carbon.
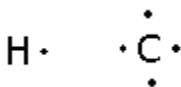
Using this notation, it is now relatively easy to represent the shared electron pairs and the carbon atom valence shell octets in methane and ethane.

Linking bonded atoms together and pairing the valence shell electrons from each gives [link].

```
    H                    H  H
    ··                   ··  ··
H : C : H           H : C : C : H
    ··                   ··  ··
    H                    H  H
```
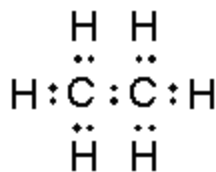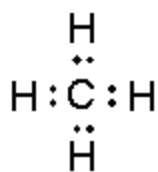
Recall that each shared pair of electrons represents a chemical bond. These are examples of what are called **Lewis structures**, after G.N. Lewis who first invented this notation. These structures reveal, at a glance, which atoms are bonded to which, i.e. the structural formula of the molecule. We can also easily count the number of valence shell electrons around each atom in the bonded molecule. Consistent with our model of the octet rule, each carbon atom has eight valence electrons and each hydrogen has two in the molecule.

In a larger hydrocarbon, the structural formula of the molecule is generally not predictable from the number of carbon atoms and the number of hydrogen atoms, so the molecular structure must be given to deduce the Lewis structure and thus the arrangement of the electrons in the molecule. However, once given this information, it is straightforward to create a Lewis structure for molecules with the general molecular formula C_nH_{2n+2} such as propane, butane, etc. For example, the Lewis structure for "normal" butane (with all carbons linked one after another) is found here.

```
    H   H   H   H
    ··  ··  ··  ··
H : C : C : C : C : H
    ··  ··  ··  ··
    H   H   H   H
```
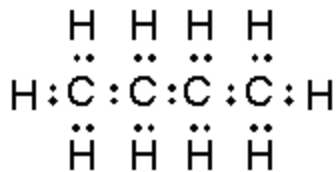
It is important to note that there exist no hydrocarbons where the number of hydrogens exceeds two more than twice the number of carbons. For example,

CH_5 does not exist, nor does C_2H_8. We correspondingly find that all attempts to draw Lewis structures which are consistent with the octet rule will fail for these molecules. Similarly, CH_3 and C_2H_5 are observed to be so extremely reactive that it is impossible to prepare stable quantities of either compound. Again we find that it is not possible to draw Lewis structures for these molecules which obey the octet rule.

We conclude from these examples that, when it is possible to draw a Lewis structure in which each carbon has a complete octet of electrons in its valence shell, the corresponding molecule will be stable and the hydrocarbon compound will exist under ordinary conditions. After working a few examples, it is apparent that this always holds for compounds with molecular formula C_nH_{2n+2}.

On the other hand, there are many stable hydrocarbon compounds with molecular formulae which do not fit the form C_nH_{2n+2}, particularly where the number of hydrogens is less than $2n+2$. In these compounds, the valences of the carbon atoms are not quite so obviously satisfied by electron pair sharing. For example, in ethene C_2H_4 and acetylene C_2H_2 there are not enough hydrogen atoms to permit each carbon atom to be bonded to four atoms each. In each molecule, the two carbon atoms must be bonded to one another. By simply arranging the electrons so that the carbon atoms share a single pair of electrons, we wind up with rather unsatisfying Lewis structures for ethene and acetylene, shown here.
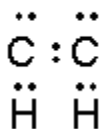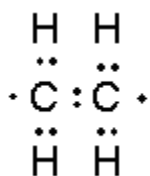
Note that, in these structures, neither carbon atom has a complete octet of valence shell electrons. Moreover, these structures indicate that the carbon-carbon bonds in ethane, ethene, and acetylene should be very similar, since in each case a single pair of electrons is shared by the two carbons. However, these bonds are observed to be chemically and physically very different. First, we can compare the energy required to break each bond (the

bond energy or **bond strength**). We find that the carbon-carbon bond energy is 347 kJ in C_2H_6, 589 kJ in C_2H_4, and 962 kJ in C_2H_2. Second, it is possible to observe the distance between the two carbon atoms, which is referred to as the **bond length**. It is found that carbon-carbon bond length is 154 pm in C_2H_6, 134 pm in C_2H_4, and 120 pm in C_2H_2. ($1\,\text{picometer} = 1\,\text{pm} = 10^{-12}m$). These observations reveal clearly that the bonding between the carbon atoms in these three molecules must be very different.

Note that the bond in ethene is about one and a half times as strong as the bond in ethane; this suggests that the two unpaired and unshared electrons in the ethene structure above are also paired and shared as a second bond between the two carbon atoms. Similarly, since the bond in acetylene is about two and a half times stronger than the bond in ethane, we can imagine that this results from the sharing of three pairs of electrons between the two carbon atoms. These assumptions produce the Lewis structures here.
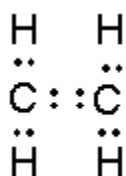
These structures appear sensible from two regards. First, the trend in carbon-carbon bond strengths can be understood as arising from the increasing number of shared pairs of electrons. Second, each carbon atom has a complete octet of electrons. We refer to the two pairs of shared electrons in ethene as a **double bond** and the three shared pairs in acetylene as a **triple bond**.

We thus extend our model of valence shell electron pair sharing to conclude that carbon atoms can bond by sharing one, two, or three pairs of electrons as needed to complete an octet of electrons, and that the strength of the bond is greater when more pairs of electrons are shared. Moreover, the data above tell us that the carbon-carbon bond in acetylene is shorter than that in ethene, which is shorter than that in ethane. We conclude that triple bonds are shorter than double bonds which are shorter than single bonds.

Observation 3: Compounds of Nitrogen, Oxygen, and the Halogens

Many compounds composed primarily of carbon and hydrogen also contain some oxygen or nitrogen, or one or more of the halogens. We thus seek to extend our understanding of bonding and stability by developing Lewis structures involving these atoms. Recall that a nitrogen atom has a valence of 3 and has five valence electrons. In our notation, we could draw a structure in which each of the five electrons appears separately in a ring, similar to what we drew for C. However, this would imply that a nitrogen atom would generally form five bonds to pair its five valence electrons. Since the valence is actually 3, our notation should reflect this. One possibility looks like this.

$$\cdot \overset{\cdot\cdot}{\underset{\cdot}{N}} \cdot$$

Note that this structure leaves three of the valence electrons "unpaired" and thus ready to join in a shared electron pair. The remaining two valence electrons are "paired," and this notation implies that they therefore are not generally available for sharing in a covalent bond. This notation is consistent with the available data, i.e. five valence electrons and a valence of 3. Pairing the two non-bonding electrons seems reasonable in analogy to the fact that electrons are paired in forming covalent bonds.

Analogous structures can be drawn for oxygen, as well as for fluorine and the other halogens, as shown here.

$$\cdot \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \cdot \qquad : \overset{\cdot\cdot}{\underset{\cdot\cdot}{F}} \cdot$$
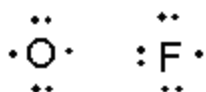
With this notation in hand, we can now analyze structures for molecules including nitrogen, oxygen, and the halogens. The hydrides are the easiest,

shown here.

H:N:H   H:O:H   H:F:
  H
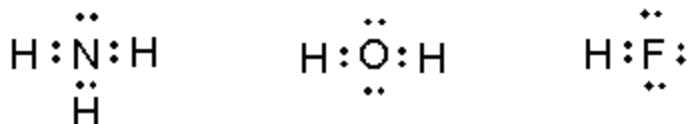
Note that the octet rule is clearly obeyed for oxygen, nitrogen, and the halogens.

At this point, it becomes very helpful to adopt one new convention: a pair of bonded electrons will now be more easily represented in our Lewis structures by a straight line, rather than two dots. Double bonds and triple bonds are represented by double and triple straight lines between atoms. We will continue to show non-bonded electron pairs explicitly.

As before, when analyzing Lewis structures for larger molecules, we must already know which atoms are bonded to which. For example, two very different compounds, ethanol and dimethyl ether, both have molecular formula C_2H_6O. In ethanol, the two carbon atoms are bonded together and the oxygen atom is attached to one of the two carbons; the hydrogens are arranged to complete the valences of the carbons and the oxygen shown here.

```
     H   H
     |   |
H — C — C — O — H
     |   |
     H   H
```
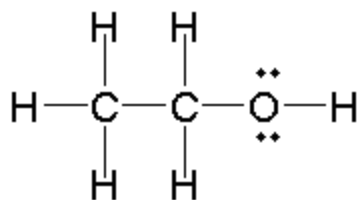
This Lewis structure reveals not only that each carbon and oxygen atom has a completed octet of valence shell electrons but also that, in the stable molecule, there are four non-bonded electrons on the oxygen atom. Ethanol is an example of an **alcohol**. Alcohols can be easily recognized in Lewis structures by the C-O-H group. The Lewis structures of all alcohols obey the octet rule.

In dimethyl ether, the two carbons are each bonded to the oxygen, in the middle, shown [here](#).

$$\text{H}-\overset{\displaystyle \overset{|}{\text{H}}}{\underset{\displaystyle \underset{|}{\text{H}}}{\text{C}}}-\overset{\displaystyle ..}{\underset{\displaystyle ..}{\text{O}}}-\overset{\displaystyle \overset{|}{\text{H}}}{\underset{\displaystyle \underset{|}{\text{H}}}{\text{C}}}-\text{H}$$
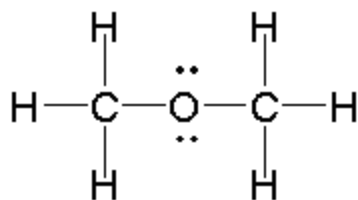
Ethers can be recognized in Lewis structures by the C-O-C arrangement. Note that, in both ethanol and dimethyl ether, the octet rule is obeyed for all carbon and oxygen atoms. Therefore, it is not usually possible to predict the structural formula of a molecule from Lewis structures. We must know the molecular structure prior to determining the Lewis structure.

Ethanol and dimethyl ether are examples of **isomers**, molecules with the same molecular formula but different structural formulae. In general, isomers have rather different chemical and physical properties arising from their differences in molecular structures.

A group of compounds called **amines** contain hydrogen, carbon, and nitrogen. The simplest amine is methyl amine, whose Lewis structure is [here](#).

$$\text{H}-\overset{\displaystyle \overset{|}{\text{H}}}{\underset{\displaystyle \underset{|}{\text{H}}}{\text{C}}}-\overset{\displaystyle ..}{\underset{\displaystyle \underset{|}{\text{H}}}{\text{N}}}-\text{H}$$
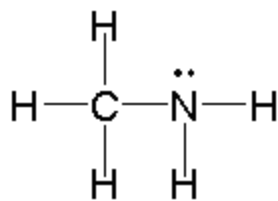
"Halogenated" hydrocarbons have been used extensively as refrigerants in air conditioning systems and refrigerators. These are the notorious "chlorofluorocarbons" or "CFCs" which have been implicated in the destruction of stratospheric ozone. Two of the more important CFCs include

Freon 11, $CF\,Cl_3$, and Freon 114, $C_2F_4\,Cl_2$, for which we can easily construct appropriate Lewis structures, shown [here](#).
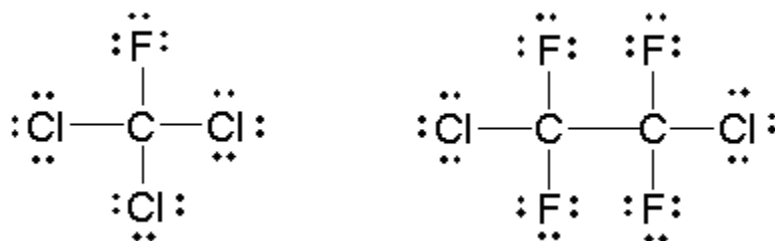
Finally, Lewis structures account for the stability of the diatomic form of the elemental halogens, F_2, Cl_2, Br_2, and I_2. The single example of F_2 is sufficient, shown [here](#).
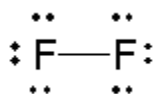
We can conclude from these examples that molecules containing oxygen, nitrogen, and the halogens are expected to be stable when these atoms all have octets of electrons in their valence shells. The Lewis structure of each molecule reveals this character explicitly.

On the other hand, there are many examples of common molecules with apparently unusual valences, including: carbon dioxide CO_2, in which the carbon is bonded to only two atoms and each oxygen is only bonded to one; formaldehyde H_2CO; and hydrogen cyanide HCN. Perhaps most conspicuously, we have yet to understand the bonding in two very important elemental diatomic molecules, O_2 and N_2, each of which has fewer atoms than the valence of either atom.

We first analyze CO_2, noting that the bond strength of one of the CO bonds in carbon dioxide is 532 kJ, which is significantly greater than the bond strength of the CO bond in ethanol, 358 kJ. By analogy to the comparison of bonds strengths in ethane to ethene, we can imagine that this

difference in bond strengths results from double bonding in CO_2. Indeed, a Lewis structure of CO_2 in which only single electron pairs are shared ([link]) does not obey the octet rule, but one in which we pair and share the extra electrons reveals that double bonding permits the octet rule to be obeyed ([link]).
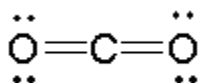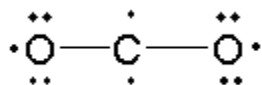
A comparison of bond lengths is consistent with our reasoning: the single CO bond in ethanol is 148 pm, whereas the double bond in CO_2 is 116.

Knowing that oxygen atoms can double-bond, we can easily account for the structure of formaldehyde. The strength of the CO bond in H_2CO is comparable to that in CO_2, consistent with the Lewis structure here.
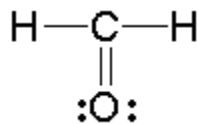
What about nitrogen atoms? We can compare the strength of the CN bond in HCN, 880 kJ, to that in methyl amine, 290 kJ. This dramatic disparity again suggests the possibility of multiple bonding, and an appropriate Lewis structure for HCN is shown here.
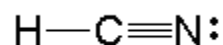
We can conclude that oxygen and nitrogen atoms, like carbon atoms, are capable of multiple bonding. Furthermore, our observations of oxygen and nitrogen reinforce our earlier deduction that multiple bonds are stronger than single bonds, and their bond lengths are shorter.

As our final examples in this section, we consider molecules in which oxygen atoms are bonded to oxygen atoms. Oxygen-oxygen bonds appear primarily in two types of molecules. The first is simply the oxygen diatomic molecule, O_2, and the second are the peroxides, typified by hydrogen peroxide, H_2O_2. In a comparison of bond energies, we find that the strength of the OO bond in O_2 is 499 kJ whereas the strength of the OO bond in H_2O_2 is 142 kJ. This is easily understood in a comparison of the Lewis structures of these molecules, showing that the peroxide bond is a single bond, whereas the O_2 bond is a double bond, shown here.
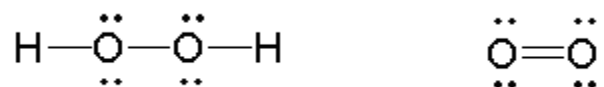
We conclude that an oxygen atom can satisfy its valence of 2 by forming two single bonds or by forming one double bond. In both cases, we can understand the stability of the resulting molecules by in terms of an octet of valence electrons.

Interpretation of Lewis Structures

Before further developing our model of chemical bonding based on Lewis structures, we pause to consider the interpretation and importance of these structures. It is worth recalling that we have developed our model based on observations of the numbers of bonds formed by individual atoms and the number of valence electrons in each atom. In general, these structures are useful for predicting whether a molecule is expected to be stable under normal conditions. If we cannot draw a Lewis structure in which each carbon, oxygen, nitrogen, or halogen has an octet of valence electrons, then the corresponding molecule probably is not stable. Consideration of bond

strengths and bond lengths enhances the model by revealing the presence of double and triple bonds in the Lewis structures of some molecules.

At this point, however, we have observed no information regarding the geometries of molecules. For example, we have not considered the angles measured between bonds in molecules. Consequently, the Lewis structure model of chemical bonding does not at this level predict or interpret these bond angles. (This will be considered here.) Therefore, although the Lewis structure of methane is drawn as shown here.
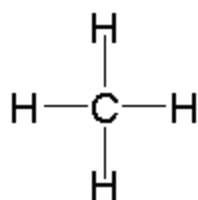
This does **not** imply that methane is a flat molecule, or that the angles between CH bonds in methane is 90°. Rather, the structure simply reveals that the carbon atom has a complete octet of valence electrons in a methane molecule, that all bonds are single bonds, and that there are no non-bonding electrons. Similarly, one can write the Lewis structure for a water molecule in two apparently different ways, shown here.
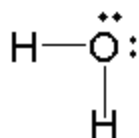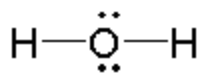
However, it is very important to realize that these two structures are **identical** in the Lewis model, because both show that the oxygen atom has a complete octet of valence electrons, forms two single bonds with hydrogen atoms, and has two pairs of unshared electrons in its valence shell. In the same way, the two structures for Freon 114 shown here are also **identical**.
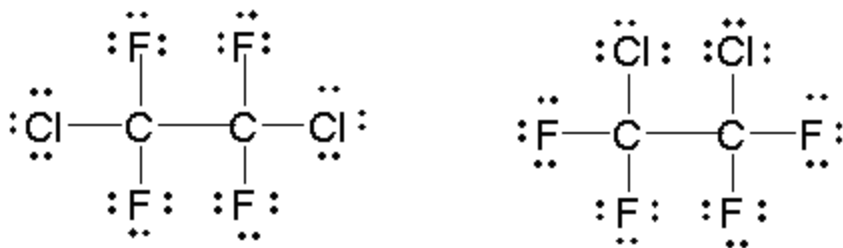
These two drawings do not represent different structures or arrangements of the atoms in the bonds.

Finally, we must keep in mind that we have drawn Lewis structures strictly as a convenient tool for our understanding of chemical bonding and molecular stability. It is based on commonly observed trends in valence, bonding, and bond strengths. These structures must not be mistaken as observations themselves, however. As we encounter additional experimental observations, we must be prepared to adapt our Lewis structure model to fit these observations, but we must never adapt our observations to fit the Lewis model.

Extensions of the Lewis Structure Model

With these thoughts in mind, we turn to a set of molecules which challenge the limits of the Lewis model in describing molecular structures. First, we note that there are a variety of molecules for which atoms clearly must bond in such a way as to have more than eight valence electrons. A conspicuous example is SF_6, where the sulfur atom is bonded to six F atoms. As such, the S atom must have 12 valence shell electrons to form 6 covalent bonds. Similarly, the phosphorous atom in PCl_5 has 10 valence electrons in 5 covalent bonds, the Cl atom in ClF_3 has 10 valence electrons in 3 covalent bonds and two lone pairs. We also observe the interesting compounds of the noble gas atoms, e.g. XeO_3, where noble gas atom begins with eight valence electrons even before forming any bonds. In each of these cases, we note that the valence of the atoms S, P, Cl, and Xe are normally 2, 3, 1, and 0, yet more bonds than this are formed. In such cases, it is not possible to draw Lewis structures in which S, P, Cl, and Xe obey the octet rule. We refer to these molecules as "expanded valence" molecules, meaning that the valence of the central atom has expanded beyond the expected octet.

There are also a variety of molecules for which there are too few electrons to provide an octet for every atom. Most notably, Boron and Aluminum, from Group III, display bonding behavior somewhat different than we have seen and thus less predictable from the model we have developed so far. These atoms have three valence shell electrons, so we might predict a valence of 5 on the basis of the octet rule. However, compounds in which boron or aluminum atoms form five bonds are never observed, so we must conclude that simple predictions based on the octet rule are not reliable for Group III.

Consider first boron trifluoride, BF_3. The bonding here is relatively simple to model with a Lewis structure if we allow each valence shell electron in the boron atom to be shared in a covalent bond with each fluorine atom.
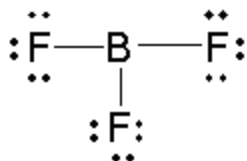
Note that, in this structure, the boron atom has only six valence shell electrons, but the octet rule is obeyed by the fluorine atoms.

We might conclude from this one example that boron atoms obey a sextet rule. However, boron will form a stable ion with hydrogen, BH_4^-, in which the boron atom does have a complete octet. In addition, BF_3 will react with ammonia NH_3 for form a stable compound, NH_3BF_3, for which a Lewis structure can be drawn in which boron has a complete octet, shown here.
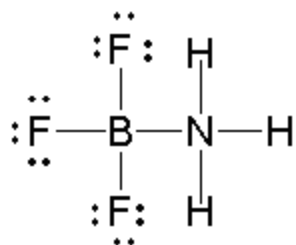
Compounds of aluminum follow similar trends. Aluminum trichloride, $Al\,Cl_3$, aluminum hydride, $Al\,H_3$, and aluminum hydroxide, $Al\,(OH)_3$, all indicate a valence of 3 for aluminum, with six valence electrons in the bonded molecule. However, the stability of aluminum hydride ions, $Al\,H_4^-$, indicates that Al can also support an octet of valence shell electrons as well.

We conclude that, although the octet rule can still be of some utility in understanding the chemistry of Boron and Aluminum, the compounds of these elements are less predictable from the octet rule. This should not be disconcerting, however. The octet rule was developed in [link] on the basis of the observation that, for elements in Groups IV through VIII, the number of valence electrons plus the most common valence is equal to eight. Elements in Groups I, II, and III do not follow this observation most commonly.

Resonance Structures

Another interesting challenge for the Lewis model we have developed is the set of molecules for which it is possible to draw more than one structure in agreement with the octet rule. A notable example is the nitric acid molecule, HNO_3, where all three oxygens are bonded to the nitrogen. Two structures can be drawn for nitric acid with nitrogen and all three oxygens obeying the octet rule.

In each structure, of the oxygens not bonded to hydrogen, one shares a single bond with nitrogen while the other shares a double bond with nitrogen. These two structures are not identical, unlike the two freon structures in [link], because the atoms are bonded differently in the two structures.

Review and Discussion Questions

Exercise:

Problem:

Compounds with formulae of the form C_nH_{2n+2} are often referred to as "saturated" hydrocarbons. Using Lewis structures, explain how and in what sense these molecules are "saturated."

Exercise:

Problem:

Molecules with formulae of the form C_nH_{2n+1} (e.g. CH_3, C_2H_5) are called "radicals" and are extremely reactive. Using Lewis structures, explain the reactivity of these molecules.

Exercise:

Problem:

State and explain the experimental evidence and reasoning which shows that multiple bonds are stronger and shorter than single bonds.

Exercise:

Problem:

Compare N_2 to H_4N_2. Predict which bond is stronger and explain why.

Exercise:

Problem:

Explain why the two Lewis structures for Freon 114, shown in Figure 21[link], are identical. Draw a Lewis structures for an isomer of Freon 114, that is, another molecule with the same molecular formula as Freon 114 but a different structural formula.

Molecular Geometry and Electron Domain Theory

Foundation

We begin by assuming a **Lewis structure model** for chemical bonding based on valence shell electron pair sharing and the octet rule. We thus assume the nuclear structure of the atom, and we further assume the existence of a valence shell of electrons in each atom which dominates the chemical behavior of that atom. A covalent chemical bond is formed when the two bonded atoms share a pair of valence shell electrons between them. In general, atoms of Groups IV through VII bond so as to complete an octet of valence shell electrons. A number of atoms, including C, N, O, P, and S, can form double or triple bonds as needed to complete an octet. We know that double bonds are generally stronger and have shorter lengths than single bonds, and triple bonds are stronger and shorter than double bonds.

Goals

We should expect that the properties of molecules, and correspondingly the substances which they comprise, should depend on the details of the structure and bonding in these molecules. The relationship between bonding, structure, and properties is comparatively simple in **diatomic** molecules, which contain two atoms only, e.g. H Cl or O_2. A **polyatomic** molecule contains more than two atoms. An example of the complexities which arise with polyatomic molecules is molecular geometry: how are the atoms in the molecule arranged with respect to one another? In a diatomic molecule, only a single molecular geometry is possible since the two atoms must lie on a line. However, with a triatomic molecule (three atoms), there are two possible geometries: the atoms may lie on a line, producing a linear molecule, or not, producing a bent molecule. In molecules with more than three atoms, there are many more possible geometries. What geometries are actually observed? What determines which geometry will be observed in a particular molecule? We seek a model which allows us to understand the observed geometries of molecules and thus to predict these geometries.

Once we have developed an understanding of the relationship between molecular structure and chemical bonding, we can attempt an understanding

of the relationship of he structure and bonding in a polyatomic molecule to the physical and chemical properties we observe for those molecules.

Observation 1: Geometries of molecules

The geometry of a molecule includes a description of the arrangements of the atoms in the molecule. At a simple level, the molecular structure tells us which atoms are bonded to which. At a more detailed level, the geometry includes the lengths of all of these bonds, that is, the distances between the atoms which are bonded together, and the angles between pairs of bonds. For example, we find that in water, H_2O, the two hydrogens are bonded to the oxygen and each O-H bond length is 95.72pm (where $1\,\mathrm{pm} = 10^{-12}m$). Furthermore, H_2O is a bent molecule, with the H-O-H angle equal to 104.5°. (The measurement of these geometric properties is difficult, involving the measurement of the frequencies at which the molecule rotates in the gas phase. In molecules in crystalline form, the geometry of the molecule is revealed by irradiating the crystal with x-rays and analyzing the patterns formed as the x-rays diffract off of the crystal.)

Not all triatomic molecules are bent, however. As a common example, CO_2 is a linear molecule. Larger polyatomics can have a variety of shapes, as illustrated in [link]. Ammonia, NH_3, is a pyramid-shaped molecule, with the hydrogens in an equilateral triangle, the nitrogen above the plane of this triangle, and a H-N-H angle equal to 107°. The geometry of CH_4 is that of a tetrahedron, with all H-C-H angles equal to 109.5°. (See also [link].) Ethane, C_2H_6, has a geometry related to that of methane. The two carbons are bonded together, and each is bonded to three hydrogens. Each H-C-H angle is 109.5° and each H-C-C angle is 109.5°. By contrast, in ethene, C_2H_4, each H-C-H bond angle is 116.6° and each H-C-C bond angle is 121.7°. All six atoms of ethene lie in the same plane. Thus, ethene and ethane have very different geometries, despite the similarities in their molecular formulae.
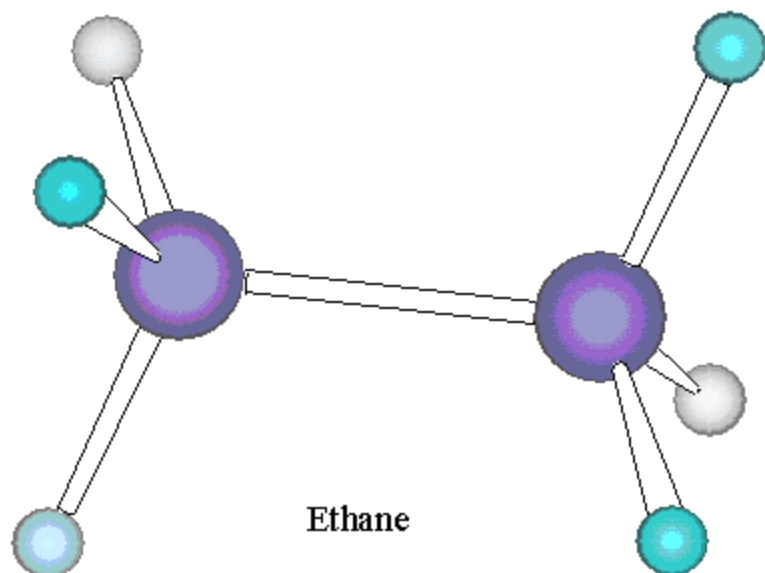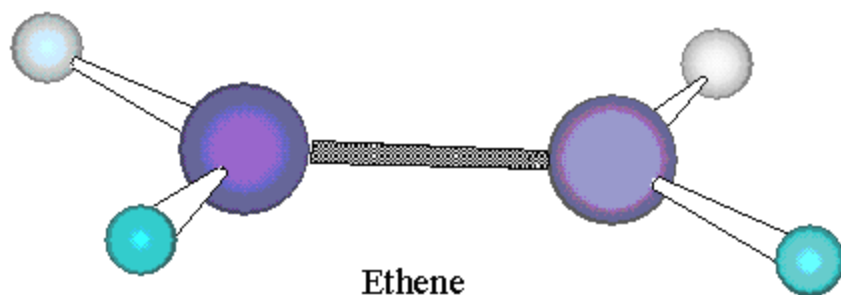Molecular Structures
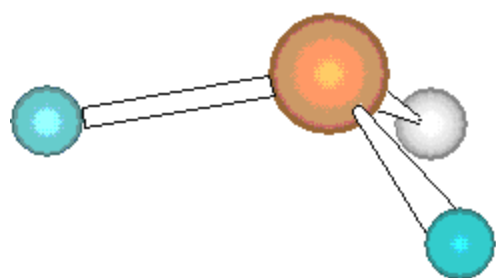
Ammonia
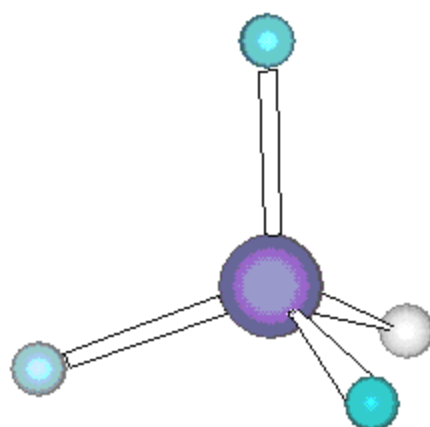
Methane

Ethane

Ethene

We begin our analysis of these geometries by noting that, in the molecules listed above which do **not** contain double or triple bonds (H_2O, NH_3, CH_4 and C_2H_6), the bond angles are very similar, each equal to or very close to the tetrahedral angle 109.5°. To account for the observed angle, we begin with our valence shell electron pair sharing model, and we note that, in the Lewis structures of these molecules, the central atom in each bond angle of these molecules contains four pairs of valence shell electrons. For methane and ethane, these four electron pairs are all shared with adjacent bonded atoms, whereas in

ammonia or water, one or two (respectively) of the electron pairs are not shared with any other atom. These unshared electron pairs are called **lone pairs** . Notice that, in the two molecules with no lone pairs, all bond angles are **exactly** equal to the tetrahedral angle, whereas the bond angles are only close in the molecules with lone pairs

One way to understand this result is based on the mutual repulsion of the negative charges on the valence shell electrons. Although the two electrons in each bonding pair must remain relatively close together in order to form the bond, different pairs of electrons should arrange themselves in such a way that the distances between the pairs are as large as possible. Focusing for the moment on methane, the four pairs of electrons must be equivalent to one another, since the four C-H bonds are equivalent, so we can assume that the electron pairs are all the same distance from the central carbon atom. How can we position four electron pairs at a fixed distance from the central atom but as far apart from one another as possible? A little reflection reveals that this question is equivalent to asking how to place four points on the surface of a sphere spread out from each other as far apart as possible. A bit of experimentation reveals that these four points must sit at the corners of a tetrahedron, an equilateral triangular pyramid, as may be seen in [link]. If the carbon atom is at the center of this tetrahedron and the four electron pairs at placed at the corners, then the hydrogen atoms also form a tetrahedron about the carbon. This is, as illustrated in [link], the correct geometry of a methane molecule. The angle formed by any two corners of a tetrahedron and the central atom is 109.5°, exactly in agreement with the observed angle in methane. This model also works well in predicting the bond angles in ethane.

Tetrahedral Structure of Methane
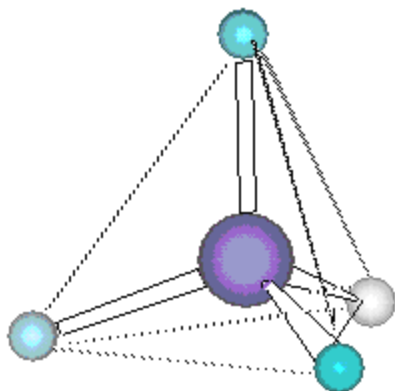
The dotted lines illustrate that the hydrogens form a tetrahedron about the carbon atom.
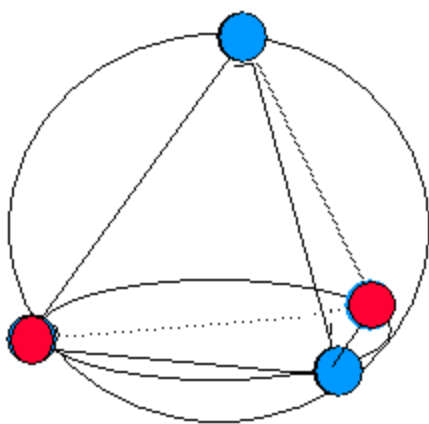
The same tetrahedron is formed by placing four points on a sphere as far apart from one another as possible.

We conclude that molecular geometry is determined by minimizing the mutual repulsion of the valence shell electron pairs. As such, this model of molecular geometry is often referred to as the **valence shell electron pair repulsion (VSEPR) theory** . For reasons that will become clear, extension of this model implies that a better name is the **Electron Domain (ED) Theory** .

This model also accounts, at least approximately, for the bond angles of H_2O and NH_3. These molecules are clearly not tetrahedral, like CH_4, since neither contains the requisite five atoms to form the tetrahedron. However, each molecule does contain a central atom surrounded by four pairs of valence shell electrons. We expect from our Electron Domain model that those four pairs should be arrayed in a tetrahedron, without regard to whether they are bonding or lone-pair electrons. Then attaching the hydrogens (two for oxygen, three for nitrogen) produces a prediction of bond angles of 109.5°, very close indeed to the observed angles of 104.5° in H_2O and 107° in NH_3.

Note, however, that we do not describe the geometries of H_2O and NH_3 as "tetrahedral," since the **atoms** of the molecules do not form tetrahedrons, even if the valence shell electron pairs do. (It is worth noting that these angles are not exactly equal to 109.5°, as in methane. These deviations will be discussed later.)

We have developed the Electron Domain model to this point only for geometries of molecules with four pairs of valence shell electrons. However, there are a great variety of molecules in which atoms from Period 3 and beyond can have more than an octet of valence electrons. We consider two such molecules illustrated in [link].
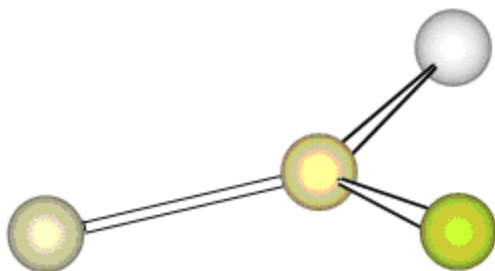More Molecular Structures
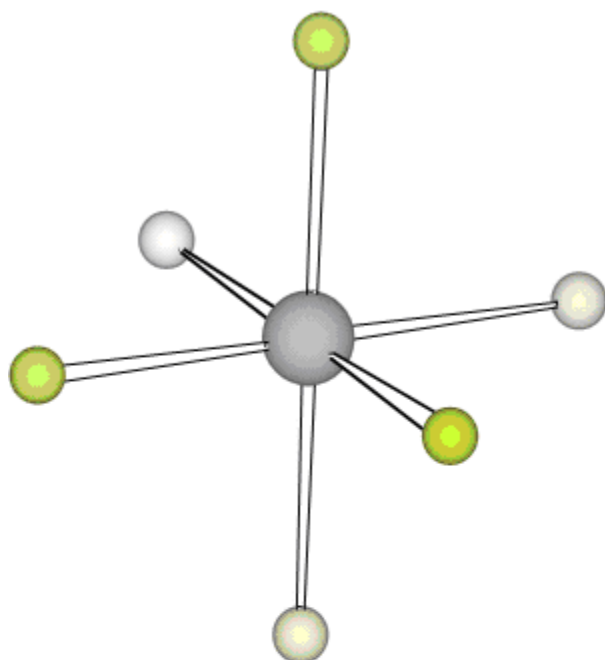
Sulfur Hexafluoride
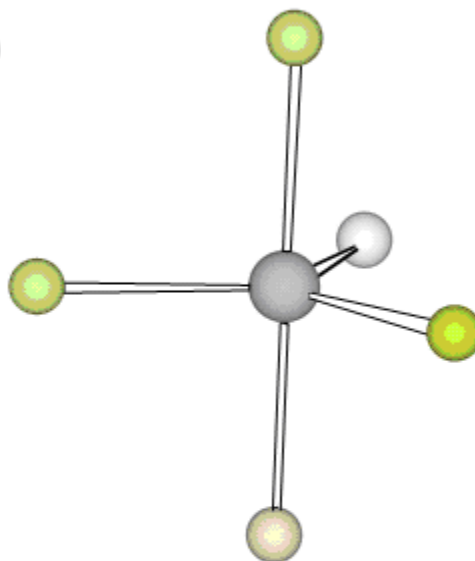
Phosphorous Pentachloride

Boron Trichloride

First, PCl_5 is a stable gaseous compound in which the five chlorine atoms are each bonded to the phosphorous atom. Experiments reveal that the geometry of PCl_5 is that of a **trigonal bipyramid** : three of the chlorine atoms form an equilateral triangle with the P atom in the center, and the other two chlorine atoms are on top of and below the P atom. Thus there must be 10 valence shell electrons around the phosphorous atom. Hence, phosphorous exhibits what is called an **expanded valence** in PCl_5. Applying our Electron Domain model, we expect the five valence shell

electron pairs to spread out optimally to minimize their repulsions. The required geometry can again be found by trying to place five points on the surface of a sphere with maximum distances amongst these points. A little experimentation reveals that this can be achieved by placing the five points to form a trigonal bipyramid. Hence, Electron Domain theory accounts for the geometry of PCl_5.

Second, SF_6 is a fairly unreactive gaseous compound in which all six fluorine atoms are bonded to the central sulfur atom. Again, it is clear that the octet rule is violated by the sulfur atom, which must therefore have an expanded valence. The observed geometry of SF_6, as shown in [link], is highly symmetric: all bond lengths are identical and all bond angles are 90°. The F atoms form an **octahedron** about the central S atom: four of the F atoms form a square with the S atom at the center, and the other two F atoms are above and below the S atom. To apply our Electron Domain model to understand this geometry, we must place six points, representing the six electron pairs about the central S atom, on the surface of a sphere with maximum distances between the points. The requisite geometry is found, in fact, to be that of an octahedron, in agreement with the observed geometry.

As an example of a molecule with an atom with less than an octet of valence shell electrons, we consider boron trichloride, BCl_3. The geometry of BCl_3 is also given in [link]: it is **trigonal planar** , with all four atoms lying in the same plane, and all Cl-B-Cl bond angles equal to 120°. The three Cl atoms form an equilateral triangle. The Boron atom has only three pairs of valence shell electrons in BCl_3. In applying Electron Domain theory to understand this geometry, we must place three points on the surface of a sphere with maximum distance between points. We find that the three points form an equilateral triangle in a plane with the center of the sphere, so Electron Domain is again in accord with the observed geometry.

We conclude from these predictions and observations that the Electron Domain model is a reasonably accurate way to understand molecular geometries, even in molecules which violate the octet rule.

Observation 2: Molecules with Double or Triple Bonds

In each of the molecules considered up to this point, the electron pairs are either in single bonds or in lone pairs. In current form, the Electron Domain model does **not** account for the observed geometry of C_2H_4, in which each H-C-H bond angle is 116.6° and each H-C-C bond angle is 121.7° and all six atoms lie in the same plane. Each carbon atom in this molecule is surrounded by four pairs of electrons, all of which are involved in bonding, i.e. there are no lone pairs. However, the arrangement of these electron pairs, and thus the bonded atoms, about each carbon is not even approximately tetrahedral. Rather, the H-C-H and H-C-C bond angles are much closer to 120°, the angle which would be expected if **three** electron pairs were separated in the optimal arrangement, as just discussed for BCl_3.

This observed geometry can be understood by re-examining the Lewis structure. Recall that, although there are four electron pairs about each carbon atom, two of these pairs form a double bond between the carbon atoms. It is tempting to assume that these four electron pairs are forced apart to form a tetrahedron as in previous molecules. However, if this were this case, the two pairs involved in the double bond would be separated by an angle of 109.5° which would make it impossible for both pairs to be localized between the carbon atoms. To preserve the double bond, we must assume that the two electron pairs in the double bond remain in the same vicinity. Given this assumption, separating the three **independent** groups of electron pairs about a carbon atom produces an expectation that all three pairs should lie in the same plane as the carbon atom, separated by 120° angles. This agrees very closely with the observed bond angles. We conclude that the our model can be extended to understanding the geometries of molecules with double (or triple) bonds by treating the multiple bond as two electron pairs confined to a single **domain**. It is for this reason that we refer to the model as Electron Domain theory.

Applied in this form, Electron Domain theory can help us understand the linear geometry of CO_2. Again, there are four electron pairs in the valence shell of the carbon atom, but these are grouped into only two domains of two electron pairs each, corresponding to the two C=O double bonds. Minimizing the repulsion between these two domains forces the oxygen atoms to directly opposite sides of the carbon, producing a linear molecule.

Similar reasoning using Electron Domain theory as applied to triple bonds correctly predicts that acetylene, $HCCH$, is a linear molecule. If the electron pairs in the triple bond are treated as a single domain, then each carbon atom has only two domains each. Forcing these domains to opposite sides from one another accurately predicts 180° H-C-C bond angles.

Observation 3: Distortions from Expected Geometries

It is interesting to note that some molecular geometries (CH_4, CO_2, $HCCH$) are exactly predicted by the Electron Domain model, whereas in other molecules, the model predictions are only approximately correct. For examples, the observed angles in ammonia and water each differ slightly from the tetrahedral angle. Here again, there are four pairs of valence shell electrons about the central atoms. As such, it is reasonable to conclude that the bond angles are determined by the mutual repulsion of these electron pairs, and are thus expected to be 109.5°, which is close but not exact.

One clue as to a possible reason for the discrepancy is that the bond angles in ammonia and water are both **less** than 109.5°. Another is that both ammonia and water molecules have lone pair electrons, whereas there are no lone pairs in a methane molecule, for which the Electron Domain prediction is exact. Moreover, the bond angle in water, with two lone pairs, is less than the bond angles in ammonia, with a single lone pair. We can straightforwardly conclude from these observations that the lone pairs of electrons must produce a greater repulsive effect than do the bonded pairs. Thus, in ammonia, the three bonded pairs of electrons are forced together slightly compared to those in methane, due to the greater repulsive effect of the lone pair. Likewise, in water, the two bonded pairs of electrons are even further forced together by the two lone pairs of electrons.

This model accounts for the comparative bond angles observed experimentally in these molecules. The valence shell electron pairs repel one another, establishing the geometry in which the energy of their interaction is minimized. Lone pair electrons apparently generate a greater repulsion, thus slightly reducing the angles between the bonded pairs of electrons. Although this model accounts for the observed geometries, why should lone pair electrons generate a greater repulsive effect? We must

guess at a qualitative answer to this question, since we have no description at this point for where the valence shell electron pairs actually are or what it means to share an electron pair. We can assume, however, that a pair of electrons shared by two atoms must be located somewhere between the two nuclei, otherwise our concept of "sharing" is quite meaningless. Therefore, the powerful tendency of the two electrons in the pair to repel one another must be significantly offset by the localization of these electrons between the two nuclei which share them. By contrast, a lone pair of electrons need not be so localized, since there is no second nucleus to draw them into the same vicinity. Thus more free to move about the central atom, these lone pair electrons must have a more significant repulsive effect on the other pairs of electrons.

These ideas can be extended by more closely examining the geometry of ethene, C_2H_4 . Recall that each H-C-H bond angle is 116.6° and each H-C-C bond angle is 121.7°, whereas the Electron Domain theory prediction is for bond angles exactly equal to 120°. We can understand why the H-C-H bond angle is slightly less than 120° by assuming that the two pairs of electrons in the C=C double bond produce a greater repulsive effect than do either of the single pairs of electrons in the C-H single bonds. The result of this greater repulsion is a slight "pinching" of the H-C-H bond angle to less than 120°.

The concept that lone pair electrons produce a greater repulsive effect than do bonded pairs can be used to understand other interesting molecular geometries. Sulfur tetrafluoride, SF_4, is a particularly interesting example, shown in [link].
Molecular Structure of SF4
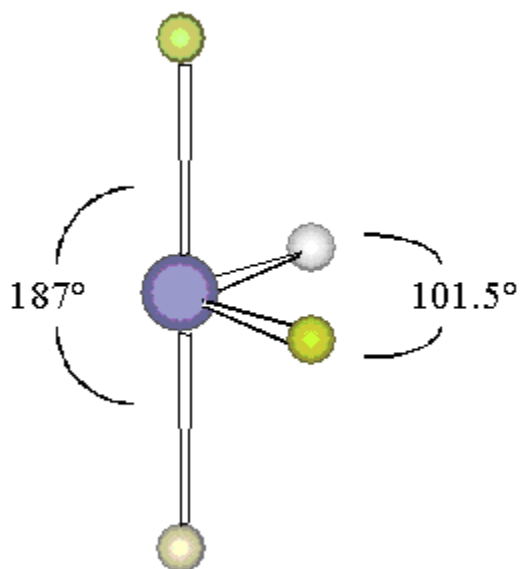
Note that two of the fluorines form close to a straight line with the central sulfur atom, but the other two are approximately perpendicular to the first two and at an angle of 101.5° to each other. Viewed sideways, this structure looks something like a seesaw.

To account for this structure, we first prepare a Lewis structure. We find that each fluorine atom is singly bonded to the sulfur atom, and that there is a lone pair of electrons on the sulfur. Thus, with five electron pairs around the central atom, we expect the electrons to arrange themselves in a trigonal bipyramid, similar to the arrangement in PCl_5 in [link]. In this case, however, the fluorine atoms and the lone pair could be arranged in two different ways with two different resultant molecular structures. The lone pair can either go on the axis of the trigonal bipyramid (i.e. "above" the sulfur) or on the equator of the bipyramid (i.e. "beside" the sulfur).

The actual molecular structure in [link] shows clearly that the lone pair goes on the equatorial position. This can be understood if we assume that the lone pair produces a greater repulsive effect than do the bonded pairs. With this assumption, we can deduce that the lone pair should be placed in the trigonal bipyramidal arrangement as far as possible from the bonded pairs. The equatorial position does a better job of this, since only two bonding pairs of electrons are at approximately 90° angles from the lone pair in this position. By contrast, a lone pair in the axial position is approximately 90° away from three bonding pairs. Therefore, our Electron Domain model

assumptions are consistent with the observed geometry of SF_4. Note that these assumptions also correctly predict the observed distortions away from the 180° and 120° angles which would be predicted by a trigonal bipyramidal arrangement of the five electron pairs.

Review and Discussion Questions

Exercise:

Problem:

Using a styrofoam or rubber ball, prove to yourself that a tetrahedral arrangement provides the maximum separation of four points on the surface of the ball. Repeat this argument to find the expected arrangements for two, three, five, and six points on the surface of the ball.

Exercise:

Problem:

Explain why arranging points on the surface of a sphere can be considered equivalent to arranging electron pairs about a central atom.

Exercise:

Problem:

The valence shell electron pairs about the central atom in each of the molecules H_2O, NH_3, and CH_4 are arranged approximately in a tetrahedron. However, only CH_4 is considered a tetrahedral molecule. Explain why these statements are not inconsistent.

Exercise:

Problem:

Explain how a comparison of the geometries of H_2O and CH_4 leads to a conclusion that lone pair electrons produce a greater repulsive effect than do bonded pairs of electrons. Give a physical reason why this might be expected.

Exercise:

Problem:

Explain why the octet of electrons about each carbon atom in ethene, C_2H_4, are not arranged even approximately in a tetrahedron.

Exercise:

Problem:

Assess the accuracy of the following reasoning and conclusions: "A trigonal bipyramid forms when there are five electron domains. If one ED is a lone pair, then the lone pair takes an equatorial position and the molecule has a seesaw geometry. If two EDs are lone pairs, we have to decide among the following options: both axial, both equatorial, or one axial and one equatorial. By placing both lone pairs in the axial positions, the lone pairs are as far apart as possible, so the trigonal planar structure is favored."

Exercise:

Problem:

Assess the accuracy of the following reasoning and conclusions: "The Cl-X-Cl bond angles in the [two molecules](#) are identical, because the bond angle is determined by the repulsion of the two Cl atoms, which is identical in the two molecules."
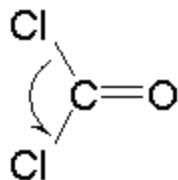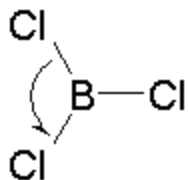
Molecular Structure and Physical Properties

Foundation

We begin with our knowledge of the structure and properties of atoms. We know that atoms have a nuclear structure, meaning that all of the positive charge and virtually all of the mass of the atom are concentrated in a nucleus which is a very small fraction of the volume of the atom. In addition, we know that many of the properties of atoms can be understood by a model in which the electrons in the atom are arranged in "shells" about the nucleus, with each shell farther from the nucleus that the previous. The electrons in outer shells are more weakly attached to the atom than the electrons in the inner shells, and only a limited number of electrons can fit in each shell. Within each shell are subshells, each of which can also hold a limited number of electrons. The electrons in different subshells have different energies and different locations for motion about the nucleus. We also assume a knowledge of the a **Lewis structure** model for chemical bonding based on valence shell electron pair sharing and the octet rule. A covalent chemical bond is formed when the two bonded atoms share a pair of valence shell electrons between them. In general, atoms of Groups IV through VII bond so as to complete an octet of valence shell electrons. We finally assume the **Electron Domain Model** for understanding and predicting molecular geometries. The pairs of valence shell electrons are arranged in bonding and non-bonding domains, and these domains are separated in space to minimize electron-electron repulsions. This electron domain arrangement determines the molecular geometry.

Goals

We should expect that the properties of molecules, and correspondingly the substances which they comprise, should depend on the details of the structure and bonding in these molecules. Now that we have developed an understanding of the relationship between molecular structure and chemical bonding, we analyze physical properties of the molecules and compounds of these molecules to relate to this bonding and structure. Simple examples of physical properties which can be related to molecular properties are the

melting and boiling temperatures. These vary dramatically from substance to substance, even for substances which appear similar in molecular formulae, with some melting temperatures in the hundreds or thousands of degrees Celsius and others well below 0°C. We seek to understand these variations by analyzing molecular structures.

To develop this understanding, we will have to apply more details of our understanding of atomic structure and electronic configurations. In our covalent bonding model, we have assumed that atoms "share" electrons to form a bond. However, our knowledge of the properties of atoms reveals that different atoms attract electrons with different strengths, resulting in very strong variations in ionization energies, atomic radii, and electron affinities. We seek to incorporate this information into our understanding of chemical bonding

Observation 1: Compounds of Groups I and II

We begin by analyzing compounds formed from elements from Groups I and II (e.g. sodium and magnesium). These compounds are not currently part of our Lewis structure model. For example, Sodium, with a single valence electron, is unlikely to gain seven additional electrons to complete an octet. Indeed, the common valence of the alkali metals in Group I is 1, not 7, and the common valence of the alkaline earth metals is 2, not 6. Thus, our current model of bonding does not apply to elements in these groups.

To develop an understanding of bonding in these compounds, we focus on the halides of these elements. In [link], we compare physical properties of the chlorides of elements in Groups I and II to the chlorides of the elements of Groups IV, V, and VI, and we see enormous differences. All of the alkali halides and alkaline earth halides are solids at room temperature and have melting points in the hundreds of degrees centigrade. The melting point of $Na\,Cl$ is 808°C, for example. By contrast, the melting points of the non-metal halides from Periods 2 and 3, such as $C\,Cl_4$, $P\,Cl_3$, and $S\,Cl_2$, are below 0°C, so that these materials are liquids at room temperature. Furthermore, all of these compounds have low boiling points, typically in the range of 50°C to 80°C.

	Melting Point (°C)	Boiling Point (°C)
Li Cl	610	1382
Be Cl_2	405	488
C Cl_4	-23	77
N Cl_3	-40	71
O Cl_2	-20	4
F Cl	-154	-101
Na Cl	808	1465
Mg Cl_2	714	1418
Si Cl_4	-68	57
P Cl_3	-91	74
S Cl_2	-122	59
Cl_2	-102	-35
K Cl	772	1407
Ca Cl_2	772	>1600

Melting Points and Boiling Points of Chloride Compounds

Second, the non-metal halide liquids are electrical insulators, that is, they do not conduct an electrical current. By contrast, when we melt an alkali halide or alkaline earth halide, the resulting liquid is an excellent electrical conductor. This indicates that these molten compounds consist of ions, whereas the non-metal halides do not.

We must conclude that the bonding of atoms in alkali halides and alkaline earth halides differs significantly from bonding in non-metal halides. We need to extend our valence shell electron model to account for this bonding, and in particular, we must account for the presence of ions in the molten metal halides. Consider the prototypical example of $NaCl$. We have already deduced that Cl atoms react so as to form a complete octet of valence shell electrons. Such an octet could be achieved by covalently sharing the single valence shell electron from a sodium atom. However, such a covalent sharing is clearly inconsistent with the presence of ions in molten sodium chloride. Furthermore, this type of bond would predict that $NaCl$ should have similar properties to other covalent chloride compounds, most of which are liquids at room temperature. By contrast, we might imagine that the chlorine atom completes its octet by taking the valence shell electron from a sodium atom, without covalent sharing. This would account for the presence of Na^+ and Cl^- ions in molten sodium chloride.

In the absence of a covalent sharing of an electron pair, though, what accounts for the stability of sodium chloride as a compound? It is relatively obvious that a negatively charged chloride ion will be attracted electrostatically to a positively charged sodium ion. We must also add to this model, however, the fact that individual molecules of $NaCl$ are not generally observed at temperatures less than 1465°C, the boiling point of sodium chloride. Note that, if solid sodium chloride consists of individual sodium ions in proximity to individual chloride ions, then each positive ion is not simply attracted to a single specific negative ion but rather to all of the negative ions in its near vicinity. Hence, solid sodium chloride cannot be viewed as individual $NaCl$ molecules, but must be viewed rather as a lattice of positive sodium ions interacting with negative chloride ions. This type of "ionic" bonding, which derives from the electrostatic attraction of interlocking lattices of positive and negative ions, accounts for the very high melting and boiling points of the alkali halides.

We can now draw modified Lewis structures to account for ionic bonding, but these are very different from our previous drawings. Sodium chloride can be represented as shown in [link].

$$(\text{Na}^+) \, (\, \ddot{\underset{\cdot\cdot}{\text{Cl}}} \, \colon \, ^-)$$
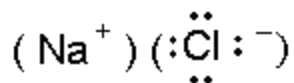
This indicates explicitly that the bonding is due to positive-negative ion attraction, and not due to sharing of an electron pair. The only sense in which the Na^+ ion has obeyed an octet rule is perhaps that, in having emptied its valence shell of electrons, the remaining outer shell of electrons in the ion has the same octet as does a neon atom. We must keep in mind, however, that the positive sodium ion is attracted to many negative chloride ions, and not just the single chloride ion depicted in the Lewis structure.

Observation 2: Molecular Dipole Moments

Our Lewis model of bonding, as currently developed, incorporates two extreme views of the distribution of electrons in a bond. In a covalent bond, we have assumed up to this point that the electron pair is shared perfectly. In complete contrast, in ionic bonding we have assumed that the electrons are not shared at all. Rather, one of the atoms is assumed to entirely extract one or more electrons from the other. We might expect that a more accurate description of the reality of chemical bonds falls in general somewhere between these two extremes. To observe this intermediate behavior, we can examine molecular dipole moments.

An electric dipole is a spatial separation of positive and negative charges. In the simplest case, a positive charge Q and a negative charge $-Q$ separated by a distance R produce a measurable **dipole moment**, μ equal to $Q \times R$. An electric field can interact with an electric dipole and can even orient the dipole in the direction of the field.

We might initially expect that molecules do not in general have dipole moments. Each atom entering into a chemical bond is electrically neutral, with equal numbers of positive and negative charges. Consequently, a molecule formed from neutral atoms must also be electrically neutral. Although electron pairs are shared between bonded nuclei, this does not affect the total number of negative charges. We might from these simple statements that molecules would be unaffected by electric or magnetic fields, each molecule behaving as a single uncharged particle.

This prediction is incorrect, however. To illustrate, a stream of water can be deflected by an electrically charged object near the stream, indicating that individual water molecules exhibit a dipole moment. A water molecule is rather more complicated than a simple separation of a positive and negative charges, however. Recall though that a water molecule has equal total numbers of positive and negative charges, consisting of three positively charged nuclei surrounded by ten electrons. Nevertheless, measurements reveal that water has a dipole moment of $6.17 \times 10^{-30} \, (Cm) = 1.85$ debye. (The debye is a unit used to measure dipole moments: 1 debye $= 3.33 \times 10^{-30} \, (Cm)$.) Water is not unique: the molecules of most substances have dipole moments. A sampling of molecules and their dipole moments is given in [link].

	μ (debye)
H_2O	1.85
HF	1.91
$H\,Cl$	1.08
$H\,Br$	0.80
HI	0.42
CO	0.12
CO_2	0
NH_3	1.47
PH_3	0.58

	μ (debye)
As H_3	0.20
CH_4	0
Na Cl	9.00

Dipole Moments of Specific Molecules

Focusing again on the water molecule, how can we account for the existence of a dipole moment in a neutral molecule? The existence of the dipole moment reveals that a water molecule must have an internal separation of positive partial charge δ and negative partial charge $-\delta$. Thus, it must be true that the electrons in the covalent bond between hydrogen and oxygen are not **equally** shared. Rather, the shared electrons must spend more time in the vicinity of one nucleus than the other. The molecule thus has one region where, on average, there is a net surplus of negative charge and one region where, on average, there is a compensating surplus of positive charge, thus producing a molecular dipole. Additional observations reveal that the oxygen "end" of the molecule holds the partial negative charge. Hence, the covalently shared electrons spend more time near the oxygen atom than near the hydrogen atoms. We conclude that oxygen atoms have a greater ability to attract the shared electrons in the bond than do hydrogen atoms.

We should not be surprised by the fact that individual atoms of different elements have differing abilities to attract electrons to themselves. We have previously seen that different atoms have greatly varying ionization energies, representing great variation in the extent to which atoms cling to their electrons. We have also seen great variation in the electron affinities of atoms, representing variation in the extent to which atoms attract an added electron. We now define the **electronegativity** of an atom as the ability of the atom to attract electrons in a chemical bond. This is different than either ionization energy or electron affinity, because electronegativity is the attraction of electrons **in a chemical bond**, whereas ionization energy and electron affinity refer to removal and attachment of electrons in free atoms.

However, we can expect electronegativity to be correlated with electron affinity and ionization energy. In particular, the electronegativity of an atom arises from a combination of properties of the atom, including the size of the atom, the charge on the nucleus, the number of electrons about the nuclei, and the number of electrons in the valence shell.

Because electronegativity is an abstractly defined property, it cannot be directly measured. In fact, there are many definitions of electronegativity, resulting in many different scales of electronegativities. However, relative electronegativities can be observed indirectly by measuring molecular dipole moments: in general, the greater the dipole moment, the greater the separation of charges must be, and therefore, the less equal the sharing of the bonding electrons must be.

With this in mind, we refer back to the dipoles given in [link]. There are several important trends in these data. Note that each hydrogen halide (HF, HCl, HBr, and HI) has a significant dipole moment. Moreover, the dipole moments increase as we move **up** the periodic table in the halogen group. We can conclude that fluorine atoms have a greater electronegativity than do chlorine atoms, etc. Note also that HF has a greater dipole moment than H_2O, which is in turn greater than that of NH_3. We can conclude that electronegativity increases as we move **across** the periodic table from left to right in a single period. These trends hold generally in comparisons of the electronegativities of the individual elements. One set of relative electronegativities of atoms in the first three rows of the periodic table is given in [link].

	Χ
H	2.1
He	-

	χ
Li	1.0
Be	1.5
B	2.0
C	2.5
N	3.0
O	3.5
F	4.0
Ne	-
Na	0.9
Mg	1.2
Al	1.5
Si	1.8
P	2.1
S	2.5
Cl	3.0
Ar	-
K	0.8

	X
Ca	1.0

Electronegativities of Selected Atoms

Observation 3: Dipole Moments in Polyatomic Molecules

We might reasonably expect from our analysis to observe a dipole moment in any molecule formed from atoms with different electronegativities. Although this must be the case for a diatomic molecule, this is not necessarily true for a polyatomic molecule, i.e. one with more than two atoms. For example, carbon is more electronegative than hydrogen. However, the simplest molecule formed from carbon and hydrogen (e.g. CH_4) does **not** possess a dipole moment, as we see in [link]. Similarly, oxygen is significantly more electronegative than carbon, yet CO_2 is a non-polar molecule. An analysis of molecular dipole moments in polyatomic molecules requires us to apply our understanding of molecular geometry.

Note that each CO bond is expected to be polar, due to the unequal sharing of the electron pairs between the carbon and the oxygen. Thus, the carbon atom should have a slight positive charge and the oxygen atom a slight negative charge in each CO bond. However, since each oxygen atom should have the same net negative charge, neither end of the molecule would display a greater affinity for an electric field. Moreover, because CO_2 is linear, the dipole in one CO bond is exactly offset by the dipole in the opposite direction due to the other CO bond. As measured by an electric field from a distance, the CO_2 molecule does not appear to have separated positive and negative charges and therefore does not display polarity. Thus, in predicting molecular dipoles we must take into account both differences in electronegativity, which affect bond polarity, and overall molecular geometry, which can produce cancellation of bond polarities.

Using this same argument, we can rationalize the zero molecular dipole moments observed for other molecules, such as methane, ethene and acetylene. In each of these molecules, the individual CH bonds are polar.

However, the symmetry of the molecule produces a cancellation of these bond dipoles overall, and none of these molecules have a molecular dipole moment.

As an example of how a molecular property like the dipole moment can affect the macroscopic property of a substance, we can examine the boiling points of various compounds. The boiling point of a compound is determined by the strength of the forces between molecules of the compound: the stronger the force, the more energy is required to separate the molecules, the higher the temperature required to provide this energy. Therefore, molecules with strong intermolecular forces have high boiling points.

We begin by comparing molecules which are similar in size, such as the hydrides Si H_4, PH_3, and SH_2 from the third period. The boiling points at standard pressure for these molecules are, respectively, -111.8°C, -87.7°C, and -60.7°C. All three compounds are thus gases at room temperature and well below. These molecules have very similar masses and have exactly the same number of electrons. However, the dipole moments of these molecules are very different. The dipole moment of Si H_4, is 0.0D, the dipole moment of PH_3 is 0.58D, and the dipole moment of SH_2 is 0.97D. Note that, for these similar molecules, the higher the dipole moment, the higher the boiling point. Thus, molecules with larger dipole moments generally have stronger intermolecular forces than similar molecules with smaller dipole moments. This is because the positive end of the dipole in one molecule can interact electrostatically with the negative end of the dipole in another molecules, and vice versa.

We note, however, that one cannot generally predict from dipole moment information only the relative boiling points of compounds of very dissimilar molecules

Review and Discussion Questions

Exercise:

Problem:

Compare and contrast the chemical and physical properties of KCl and CCl_4, and compare and contrast how the chemical bonding model can be used to account for these properties.

Exercise:

Problem: Why is the dipole moment of $NaCl$ extremely large?

Exercise:

Problem: Explain why CO has a dipole moment but CO_2 does not.

Exercise:

Problem:

Explain why an atom with a high ionization energy is expected to have a high electronegativity. Explain why an atom with a high electron affinity is expected to have a high electronegativity.

Exercise:

Problem:

Would you predict that a Kr atom has high electronegativity or low electronegativity? Predict the relative electronegativity of Kr and F.

Exercise:

Problem:

Explain why S has a greater electronegativity than P but a smaller electronegativity than O.

Exercise:

Problem:

N atoms have a high electronegativity. However, N atoms have no electron affinity, meaning that N atoms do not attract electrons. Explain how and why these facts are not inconsistent.

Exercise:

Problem:

Explain why compounds formed from elements with large differences in electronegativities are ionic.

Exercise:

Problem:

Explain why ionic compounds have much higher melting points than covalent compounds.

Chemical Bonding and Molecular Energy Levels

Foundation

Our basis for understanding chemical bonding and the structures of molecules is the electron orbital description of the structure and valence of atoms, as provided by quantum mechanics. We assume an understanding of the periodicity of the elements based on the nuclear structure of the atom and our deductions concerning valence based on electron orbitals.

Goals

Our model of valence describes a chemical bond as resulting from the sharing of a pair of electrons in the valence shell of the bonded atoms. This sharing allows each atom to complete an octet of electrons in its valence shell, at least in the sense that we count the shared electrons as belonging to both atoms. However, it is not clear that this electron counting picture has any basis in physical reality. What is meant, more precisely, by the sharing of the electron pair in a bond, and why does this result in the bonding of two atoms together? Indeed, what does it mean to say that two atoms are bound together? Furthermore, what is the significance of sharing a pair of electrons? Why aren't chemical bonds formed by sharing one or three electrons, for example?

We seek to understand how the details of chemical bonding are related to the properties of the molecules formed, particularly in terms of the strengths of the bonds formed.

Observation 1: Bonding with a Single Electron

We began our analysis of the energies and motions of the electrons in atoms by observing the properties of the simplest atom, hydrogen, with a single electron. Similarly, to understand the energies and motions of electrons which lead to chemical bonding, we begin our observations with the simplest particle with a chemical bond, which is the H_2^+ molecular ion. Each hydrogen nucleus has a charge of +1. An H_2^+ molecular ion therefore

has a single electron. It seems inconsistent with our notions of valence that a single electron, rather than an electron pair, can generate a chemical bond. However, these concepts have been based on observations on molecules, not molecular ions like H_2^+. And it is indeed found that H_2^+ is a stable bound molecular ion.

What forces and motions hold the two hydrogen nuclei close together in the H_2^+ ion? It is worth keeping in mind that the two nuclei must repel one another, since they are both positively charged. In the absence of the electron, the two nuclei would accelerate away from one another, rather than remaining in close proximity. What is the role of the electron? Clearly, the electron is attracted to both nuclei at the same time, and, in turn, each nucleus is attracted to the electron. The effect of this is illustrated in Fig. 1. In Fig. 1a, the electron is "outside" of the two nuclei. In this position, the electron is primarily attracted to the nucleus on the left, to which it is closer. More importantly, the nucleus on the right feels a greater repulsion from the other nucleus than attraction to the electron, which is farther away. As a result, the nucleus on the right experiences a strong force driving it away from the hydrogen atom on the left. This arrangement does not generate chemical bonding, therefore. By contrast, in Fig. 1b, the electron is between the two nuclei. In this position, the electron is roughly equally attracted to the two nuclei, and very importantly, each nucleus feels an attractive force to the electron which is greater than the repulsive force generated by the other nucleus. Focusing on the electron's energy, the proximity of the two nuclei provides it a doubly attractive environment with a very low potential energy. If we tried to pull one of the nuclei away, this would raise the potential energy of the electron, since it would lose attraction to that nucleus. Hence, to pull one nucleus away requires us to add energy to the molecular ion. This is what is meant by a chemical bond: the energy of the electrons is lower when the atoms are in close proximity than when the atoms are far part. This "holds" the nuclei close together, since we must do work (add energy) to take the nuclei apart.

Figure 1

Electrostatic Interactions in H$_2^+$

(a) When the electron is outside of the region between the two nuclei, the repulsion of the nuclei exceeds the attraction of the electron to the nuclei, and no bonding force is expected.
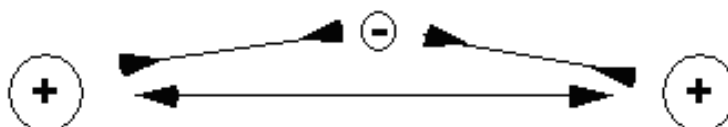
(b) When the electron is in the region between the two nuclei, the attraction of the electron to the two nuclei exceeds the repulsion of the nuclei, lowering the total energy of the molecule and producing bonding.

Note that the chemical bond in Fig. 1b results from the electron's position between the nuclei. On first thought, this appears to answer our question of what we mean by "sharing an electron pair" to form a chemical bond. An electron positioned between two nuclei is "shared" to the extent that its potential energy is lowered due to attraction to both nuclei simultaneously.

On second thought, though, this description must be inaccurate. We have learned our study of Energy Levels in Atoms that an electron must obey the

uncertainty principle and that, as a consequence, the electron does not have a definite position, between the nuclei or otherwise. We can only hope to specify a probability for observing an electron in a particular location. This probability is, from quantum mechanics, provided by the wave function. What does this probability distribution look like for the H_2^+ molecular ion?

To answer this question, we begin by experimenting with a distribution that we know: the 1s electron orbital in a hydrogen atom. This we recall has the symmetry of a sphere, with equal probability in all directions away from the nucleus. To create an H_2^+ molecular ion from a hydrogen atom, we must add a bare second hydrogen nucleus (an H^+ ion). Imagine bringing this nucleus closer to the hydrogen atom from a very great distance (see Fig. 2a). As the H^+ ion approaches the neutral atom, both the hydrogen atom's nucleus and electron respond to the electric potential generated by the positive charge. The electron is attracted and the hydrogen atom nucleus is repelled. As a result, the distribution of probability for the electron about the nucleus must become distorted, so that the electron has a greater probability of being near the H^+ ion and the nucleus has a greater probability of being farther from the ion. This distortion, illustrated in Fig. 2b, is called "polarization": the hydrogen atom has become like a "dipole", with greater negative charge to one side and greater positive charge to the other.
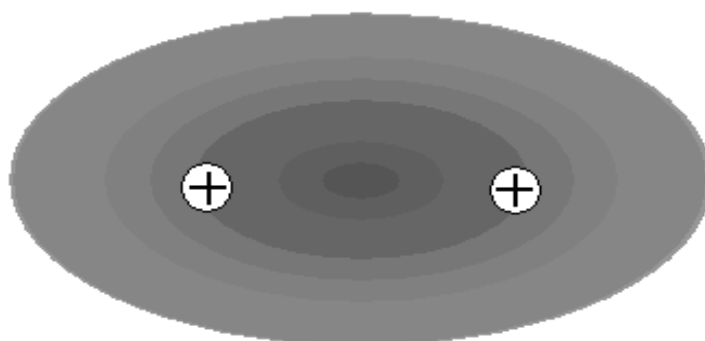
Figure 2
Polarization and Bonding in H_2^+

(a)   When the nuclei are separated to a great distance, the electron
       probability is described by a hydrogenic 1s orbital, which is
       spherical.
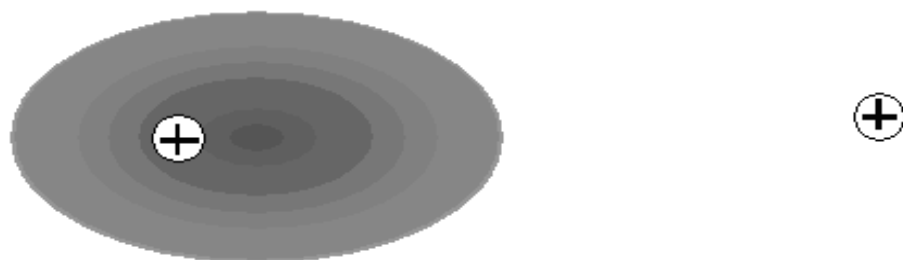
(b)   As the bare nucleus approaches the hydrogen atom, the
       electron probability becomes "polarized" in the direction of the
       positive charge.

(c)   When the nuclei are close enough together, the electron
       probability is distributed equally over both nuclei, resulting in
       a "molecular orbital."

This polarization must increase as the H^+ ion approaches the hydrogen atom until, eventually, the electron orbital must be sufficiently distorted that there is equal probability for observing the electron in proximity to either hydrogen nucleus (see Fig. 2c). The electron probability distribution in Fig. 2c now describes the motion of the electron, not in a hydrogen atom, but in an H_2^+ molecular ion. As such, we refer to this distribution as a "molecular orbital."

We note that the molecular orbital in Fig. 2c is more delocalized than the atomic orbital in Fig. 2a, and this is also important in producing the chemical bond. We recall from the discussion of Atomic Energy Levels that the energy of an electron in an orbital is determined, in part, by the compactness of the orbital. The more the orbital confines the motion of the electron, the higher is the kinetic energy of the electron, an effect we referred to as the "confinement energy." Applying this concept to the orbitals in Fig. 2, we can conclude that the confinement energy is lowered when the electron is delocalized over two nuclei in a molecular orbital. This effect contributes significantly to the lowering of the energy of an electron resulting from sharing by two nuclei.

Recall that the electron orbitals in the hydrogen atom are described by a set of quantum numbers. One of these quantum numbers is related to the symmetry or shape of the atomic orbital and is generally depicted by a letter. Recall that an "s" orbital is spherical in shape, and a "p" orbital has two lobes aligned along one axis. Similarly, the molecular orbitals for the H_2^+ molecular ion are described by a set of numbers which give the symmetry (or shape) of the orbital. For our purposes, we need only one of these descriptors, based on the symmetry of the orbital along the bond: if the molecular orbital has the symmetry of a cylinder, we refer to it as a " σ orbital." The orbital in Fig. 2c satisfies this condition.

We conclude that chemical bonding results from an electron in a molecular orbital which has substantial probability for the electron to be between two nuclei. However, this example illustrates chemical bonding with a single electron. Our rules of valence indicate that bonding typically occurs with a pair of electrons, rather than a single electron. Furthermore, this model of

bonding does not tell us how to handle molecules with many electrons (say, F_2) where most of the electrons do not participate in the bonding at all.

Observation 2: Bonding and Non-Bonding in Diatomic Molecules

We now consider molecules with more than one electron. These are illustrated most easily by diatomic molecules (molecules with only two atoms) formed by like atoms, beginning with the hydrogen molecule, H_2. The most direct experimental observation of a chemical bond is the amount of energy required to break it. This is called the bond energy, or somewhat less precisely, the bond strength. Experimentally, it is observed that the bond energy of the hydrogen molecule H_2 is 458 kJ/mol. By contrast, the bond energy of the H_2^+ molecular ion is 269 kJ/mol. Therefore, the bond in H_2 is stronger than the bond in H_2^+. Thus, the pair of shared electrons in H_2 generates a stronger attractive force than does the single electron in H_2^+.

Before deducing an explanation of this in terms of electron orbitals, we first recall the valence shell electron pair description of the bonding in H_2. Each hydrogen atom has a single electron. By sharing these two electrons, each hydrogen atom can fill its valence shell, attaining the electron configuration of helium.

How does this translate into the electron orbital picture of electron sharing that we have just described for the H_2^+ molecular ion? There are two ways to deduce the answer to this question, and, since they are both useful, we will work through them both. The first way is to imagine that we form an H_2 molecule by starting with an H_2^+ molecular ion and adding an electron to it. As a simple approximation, we might imagine that the first electron's probability distribution (its orbital) is not affected by the addition of the second electron. The second electron must have a probability distribution describing its location in the molecule as well. We recall that, in atoms, it is possible to put two electrons into a single electron orbital, provided that the two electrons have opposite values of the spin quantum number, ms. Therefore, we expect this to be true for molecules as well, and we place the

added second electron in H_2 into the same σ orbital as the first. This results in two electrons in the region between the two nuclei, thus adding to the force of attraction of the two nuclei into the bond. This explains our observation that the bond energy of H_2 is almost (although not quite) twice the bond energy of H_2^+.

The second way to understand the electron orbital picture of H_2 is to imagine that we form the molecule by starting with two separated hydrogen atoms. Each of these atoms has a single electron in a 1s orbital. As the two atoms approach one another, each electron orbital is polarized in the direction of the other atom. Once the atoms are close enough together, these two orbitals become superimposed. Now we must recall that these orbitals describe the wave-like motion of the electron, so that, when these two wave functions overlap, they must interfere, either constructively or destructively. In Fig. 3, we see the consequences of constructive and destructive interference. We can deduce that, in H_2 the electron orbitals from the atoms must constructively interfere, because that would increase the electron probability in the region between the nuclei, resulting in bonding as before. Therefore, the σ molecular orbital describing the two electrons in H_2 can be understood as resulting from the constructive overlap of two atomic 1s electron orbitals.

We now add to our observations of diatomic molecules by noting that, of the diatomic molecules formed from like atoms of the first ten elements, H_2, Li_2, B_2, C_2, N_2, O_2, and F_2 are stable molecules with chemical bonds, whereas He_2, Be_2, and Ne_2 are not bound. In examining the electron configurations of the atoms of these elements, we discover a correspondence with which diatomic molecules are bound and which ones are not. $H, Li, B, N,$ and F all have odd numbers of electrons, so that at least one electron in each atom is unpaired. By contrast, He, Be, and Ne all have even numbers of electrons, none of which are unpaired. The other atoms, C and O both have an even number of electrons. However, as deduced in our understanding of the electron configurations in atoms, electrons will, when possible, distribute themselves into different orbitals of the same energy so as to reduce the effect of their mutual repulsion. Thus, in C and O, there are three 2p orbitals into which 2 and 4 electrons are placed, respectively. Therefore, in both atoms, there are two unpaired

electrons. We conclude that bonds will form between atoms if and only if there are unpaired electrons in these atoms.

In H_2, the unpaired electrons from the separated atoms become paired in a molecular orbital formed from the overlap of the 1s atomic electron orbitals. In the case of a hydrogen atom, then, there are of course no paired electrons in the atom to worry about. In all other atoms, there certainly are paired electrons, regardless of whether there are or are not unpaired electrons. For example, in a lithium atom, there are two paired electrons in a 1s orbital and an unpaired electron in the 2s orbital. To form Li_2, the unpaired electron from each atom can be placed into a molecular orbital formed from the overlap of the 2s atomic electron orbitals. However, what becomes of the two electrons paired in the 1s orbital in a Li atom during the bonding of Li_2?

To answer this question, we examine He_2, in which each atom begins with only the two 1s electrons. As we bring the two He atoms together from a large distance, these 1s orbitals should become polarized, as in the hydrogen atom. When the polarized 1s orbitals overlap, constructive interference will again result in a σ molecular orbital, just as in H_2. Yet, we observe that He_2 is not a stable bound molecule. The problem which prevents bonding for He_2 arises from the Pauli Exclusion Principle: only two of the four electrons in He_2 can be placed into this σ bonding molecular orbital. The other two must go into a different orbital with a different probability distribution. To deduce the form of this new orbital, we recall that the bonding orbital discussed so far arises from the constructive interference of the atomic orbitals, as shown in Fig. 3. We could, instead, have assumed destructive interference of these orbitals. Destructive interference of two waves eliminates amplitude in the region of overlap of the waves, also shown in Fig. 3. In the case of the atomic orbitals, this means that the molecular orbital formed from destructive interference decreases probability for the electron to be between in the nuclei. Therefore, it increases probability for the electron to be outside the nuclei, as in Fig. 1a. As discussed there, this arrangement for the electron does not result in bonding; instead, the nuclei repel each other and the atoms are forced apart. This orbital is thus called an anti-bonding orbital. This orbital also has the symmetry of a cylinder along the bond axis, so it is also a σorbital; to

indicate that it is an anti-bonding orbital, we designate it with an asterisk, σ^*

Figure 3
Formation of Bonding and Anti-bonding Orbitals
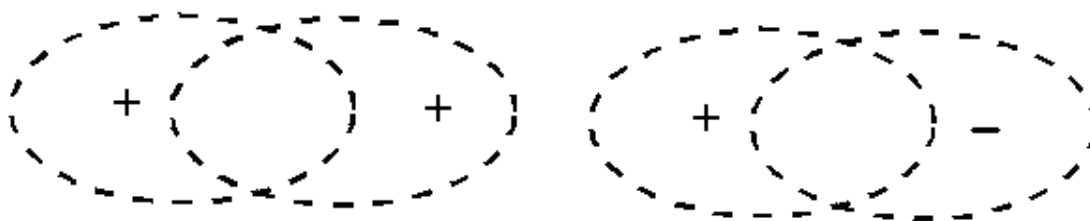
(a) When two s orbitals overlap, they can interfere constructively (same signs) or destructively (different signs).
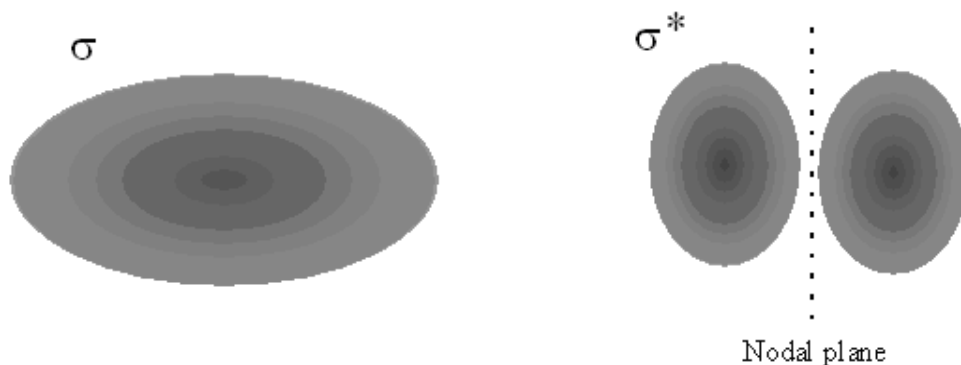
Nodal plane

(b) Constructive interference produces a bonding σ molecular orbital; destructive intereference produces an antibonding σ^* molecular orbital, with a nodal plane between the nuclei.

In He_2, both the bonding and the anti-bonding orbitals must be used in order to accommodate four electrons. The two electrons in the bonding orbital lower the energy of the molecule, but the two electrons in the anti-

bonding orbital raise it. Since two He atoms will not bind together, then the net effect must be that the anti-bonding orbital more than offsets the bonding orbital.

We have now deduced an explanation for why the paired electrons in an atom do not contribute to bonding. Both bonding and anti-bonding orbitals are always formed when two atomic orbitals overlap. When the electrons are already paired in the atomic orbitals, then there are too many electrons for the bonding molecular orbital. The extra electrons must go into the anti-bonding orbital, which raises the energy of the molecule, preventing the bond from forming.

Returning to the Li_2 example discussed above, we can develop a simple picture of the bonding. The two 1s electrons from each atom do not participate in the bonding, since the anti-bonding more than offsets the bonding. Thus, the paired "core" electrons remain in their atomic orbitals, unshared, and we can ignore them in describing the bond. The bond is formed due to overlap of the 2s orbitals and sharing of these electrons only. This is also consistent with our earlier view that the core electrons are closer to the nucleus, and thus unlikely to be shared by two atoms.

The model we have constructed seems to describe fairly well the bonding in the bound diatomic molecules listed above. For example, in a fluorine atom, the only unpaired electron is in a 2p orbital. Recall that a 2p orbital has two lobes, directed along one axis. If these lobes are assumed to lie along the axis between the two nuclei in F_2, then we can overlap them to form a bonding orbital. Placing the two unpaired electrons into this orbital then results in a single shared pair of electrons and a stable molecular bond.

Observation 3: Ionization energies of diatomic molecule

The energies of electrons in molecular orbitals can be observed directly by measuring the ionization energy. This is the energy required to remove an electron, in this case, from a molecule:

$$H_2(g) \rightarrow H_2^+(g) + e^-(g)$$
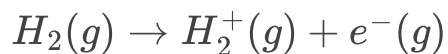
The measured ionization energy of H_2 is 1488 kJ/mol. This number is primarily important in comparison to the ionization energy of a hydrogen atom, which is 1312 kJ/mol. Therefore, it requires more energy to remove an electron from the hydrogen molecule than from the hydrogen atom, so we can conclude that the electron has a lower energy in the molecule. If we attempt to pull the atoms apart, we must raise the energy of the electron. Hence, energy is required to break the bond, so the molecule is bound.

We conclude that a bond is formed when the energy of the electrons in the molecule is lower than the energy of the electrons in the separated atoms. This conclusion seems consistent with our previous view of shared electrons in bonding molecular orbitals.

As a second example, we consider the nitrogen molecule, N_2. We find that the ionization energy of molecular nitrogen is 1503 kJ/mol, and that of atomic nitrogen is 1402 kJ/mol. Once again, we conclude that the energy of the electrons in molecular nitrogen is lower than that of the electrons in the separated atoms, so the molecule is bound.

As a third example, we consider fluorine, F_2. In this case, we find that the ionization energy of molecular fluorine is 1515 kJ/mol, which is smaller than the ionization energy of a fluorine atom, 1681 kJ/mol. This seems inconsistent with the bonding orbital concept we have developed above, which states that the electrons in the bond have a lower energy than in the separated atoms. If the electron being ionized has a higher energy in F_2 than in F, why is F_2 a stable molecule? Apparently, we need a more complete description of the molecular orbital concept of chemical bonding.

To proceed further, we compare bond energies in several molecules. Recall that the bond energy (or bond strength) is the energy required to separate the bonded atoms. We observe that the bond energy of N_2 is 956 kJ/mol. This is very much larger than the bond energy of H_2, 458 kJ/mol, and of F_2, which is 160 kJ/mol. We can account for the unusually strong bond in nitrogen using both our valence shell electron pair sharing model and our electron orbital descriptions. A nitrogen atom has three unpaired electrons in its valence shell, because the three 2p electrons distribute themselves over the three 2p orbitals, each oriented along a different axis. Each of these unpaired electrons is available for sharing with a second nitrogen atom. The

result, from valence shell electron pair sharing concepts, is that three pairs of electrons are shared between two nitrogen atoms, and we call the bond in N_2 a "triple bond." It is somewhat intuitive that the triple bond in N_2 should be much stronger than the single bond in H_2 or in F_2.

Now consider the molecular orbital description of bonding in N_2. Each of the three 2p atomic orbitals in each nitrogen atom must overlap to form a bonding molecular orbital, if we are to accommodate three electron pairs. Each 2p orbital is oriented along a single axis. One 2p orbital from each atom is oriented in the direction of the other atom, that is, along the bond axis. When these two atomic orbitals overlap, they form a molecular orbital which has the symmetry of a cylinder and which is therefore a σ orbital. Of course, they also form a σ^* orbital. The two electrons are then paired in the bonding orbital.

Figure 4
π and π^* orbitals
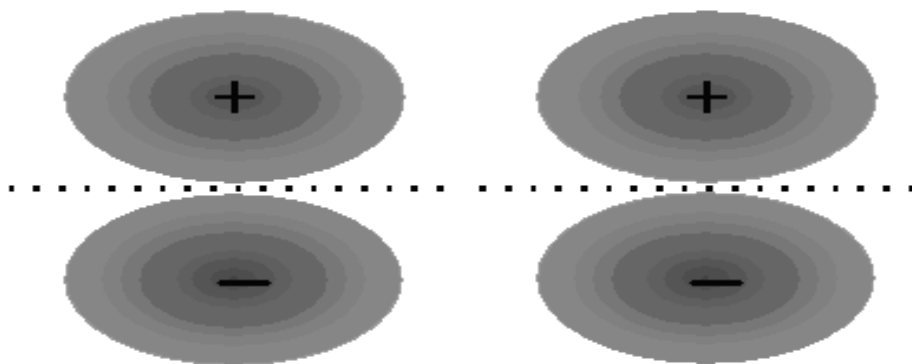
(a) Two p orbitals perpendicular to the bond axis will overlap and interfere to produce π and π^* molecular orbitals.
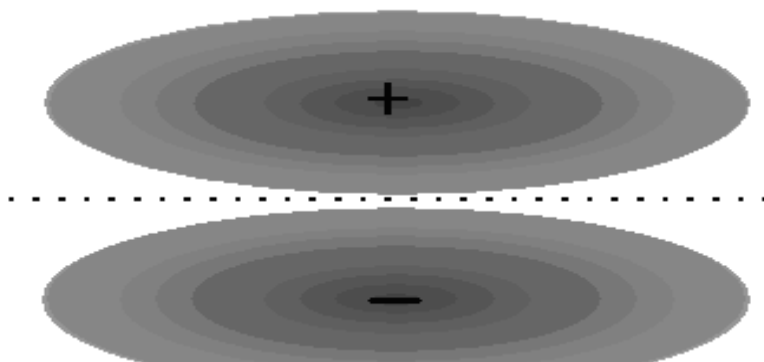
(b) Constructive interference results in formation of a bonding π molecular orbital.
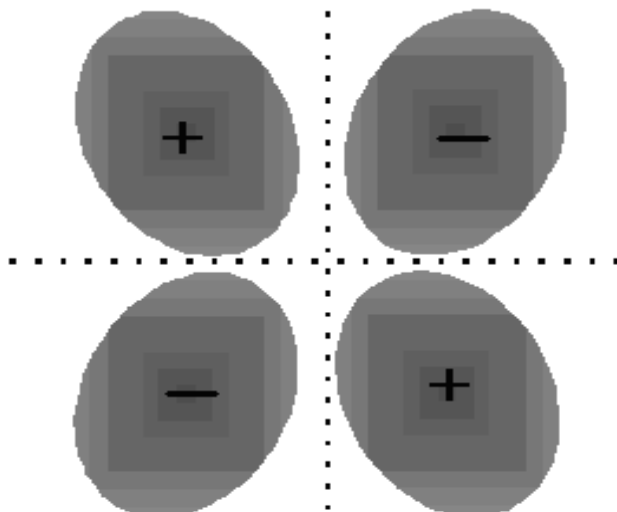

(c) Destructive interference results in formation of an anti-bonding π^* molecular orbital.

The other two 2p orbitals on each nitrogen atom are perpendicular to the bond axis. The constructive overlap between these orbitals from different atoms must therefore result in a molecular orbital somewhat different that what we have discussed before. As shown in Fig. 4, the molecular orbital which results now does not have the symmetry of a cylinder, and in fact, looks something more like a cylinder cut into two pieces. This we call a π orbital. There are two such π orbitals since there are two sets of p orbitals perpendicular to the bond axis. Figure 4 also shows that an anti-bonding orbital is formed from the destructive overlap of 2p orbitals, and this is called a π^* orbital. There are also two π^* orbitals formed from destructive overlap of 2p orbitals. In N_2, the three shared electron pairs are thus in a single σ orbital and in two π orbitals. Each of these orbitals is a bonding orbital, therefore all six electrons have their energy lowered in comparison to the separated atoms.

This is depicted in Fig. 5 in what is called a "molecular orbital energy diagram." Each pair of atomic orbitals, one from each atom, is overlapped to form a bonding and an anti-bonding orbital. The three 2p orbitals from each atom form one σ and σ^* pair and two π and π^* pairs. The lowering of

the energies of the electrons in the σ and π orbitals is apparent. The ten n=2 electrons from the nitrogen atoms are then placed pairwise, in order of increasing energy, into these molecular orbitals. Note that, in agreement with the Pauli Exclusion Principle, each pair in a single orbital consists of one spin up and one spin down electron.

Figure 5
Molecular Orbital Energy Diagram
for Nitrogen

Energy

2p σ*

2p π*

2p

2p

2p σ

2p π

2s σ*

2s

2s

2s σ
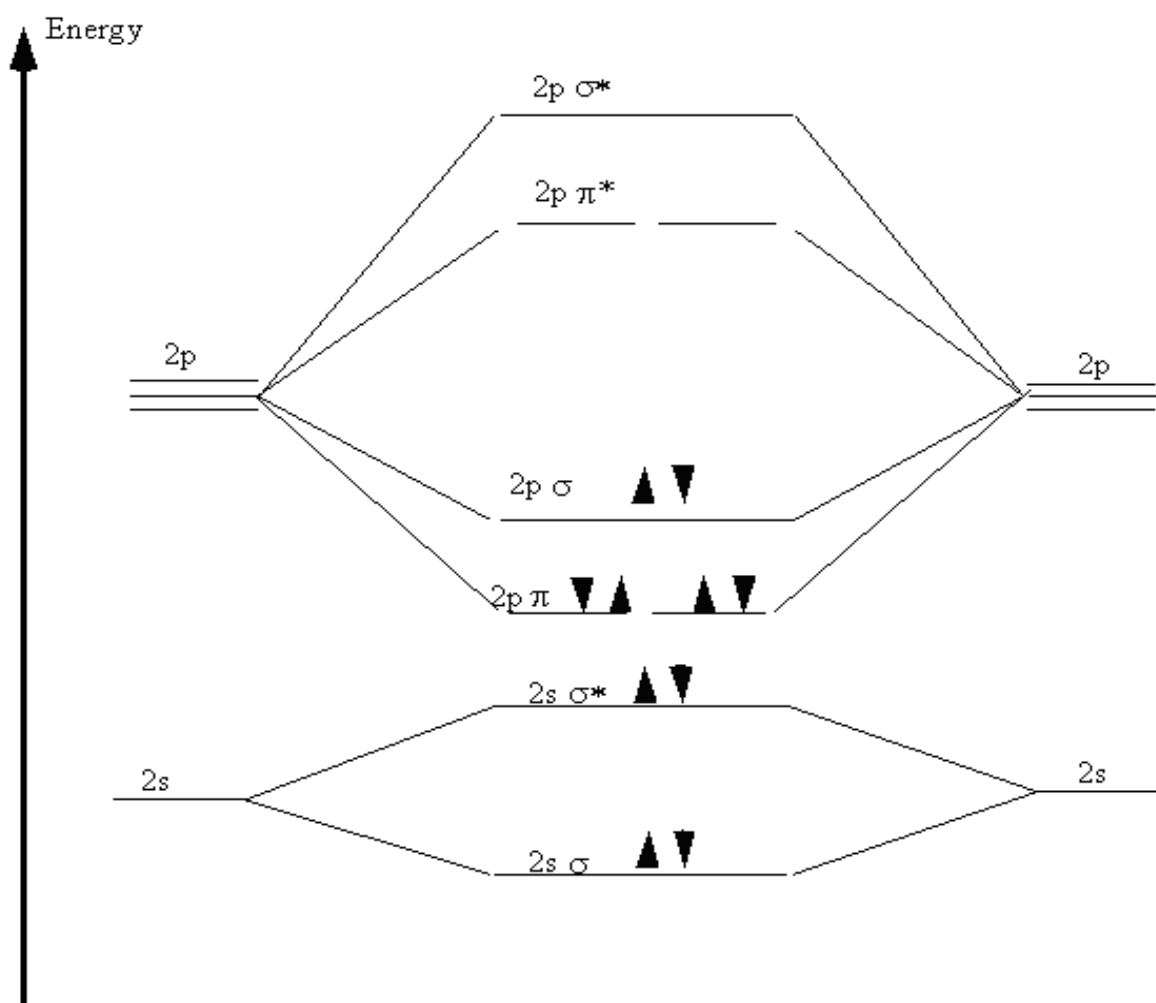
Recall now that we began the discussion of bonding in N_2 because of the curious result that the ionization energy of an electron in F_2 is less than that of an electron in an F atom. By comparing the molecular orbital energy

level diagrams for N_2 and F_2 we are now prepared to answer this puzzle. There are five p electrons in each fluorine atom. These ten electrons must be distributed over the molecular orbitals whose energies are shown in Fig. 6. (Note that the ordering of the bonding 2p orbitals differ between N_2 and F_2.) We place two electrons in the σ orbital, four more in the two π orbitals, and four more in the two π^* orbitals. Overall, there are six electrons in bonding orbitals and four in anti-bonding orbitals. Since F_2 is a stable molecule, we must conclude that the lowering of energy for the electrons in the bonding orbitals is greater than the raising of energy for the electrons in the antibonding orbitals. Overall, this distribution of electrons is, net, equivalent to having two electrons paired in a single bonding orbital.

Figure 6
Molecular Orbital Energy Diagram
## for Fluorine
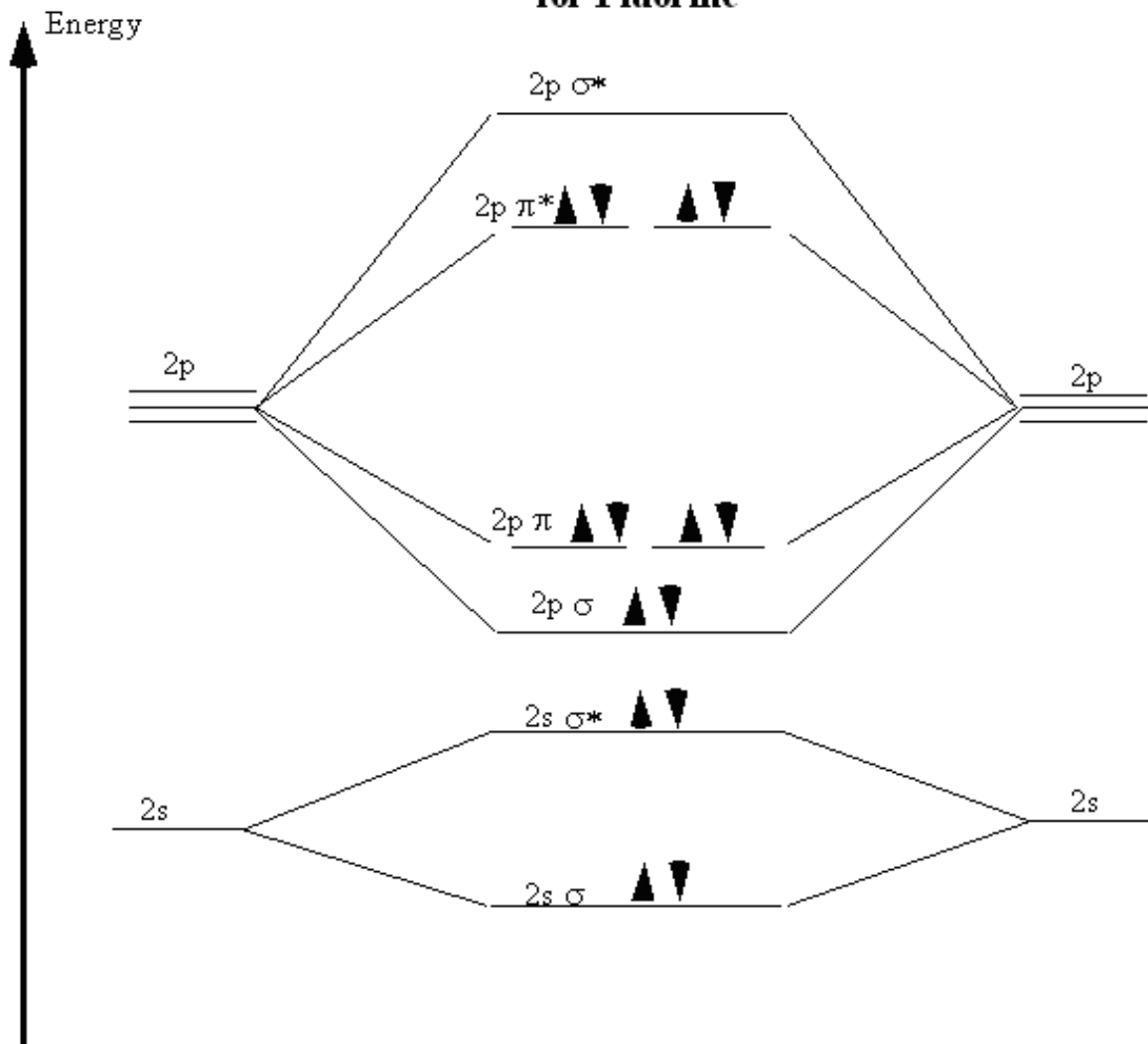
This also explains why the ionization energy of F_2 is less than that of an F atom. The electron with the highest energy requires the least energy to remove from the molecule or atom. The molecular orbital energy diagram in Fig. 6 clearly shows that the highest energy electrons in F_2 are in anti-bonding orbitals. Therefore, one of these electrons is easier to remove than an electron in an atomic 2p orbital, because the energy of an anti-bonding orbital is higher than that of the atomic orbitals. (Recall that this is why an anti-bonding orbital is, indeed, anti-bonding.) Therefore, the ionization energy of molecular fluorine is less than that of atomic fluorine. This

clearly demonstrates the physical reality and importance of the anti-bonding orbitals.

A particularly interesting case is the oxygen molecule, O_2. In completing the molecular orbital energy level diagram for oxygen, we discover that we must decide whether to pair the last two electrons in the same $2p\pi^*$ orbital, or whether they should be separated into different $2p\pi^*$ orbitals. To determine which, we note that oxygen molecules are paramagnetic, meaning that they are strongly attracted to a magnetic field. To account for this paramagnetism, we recall that electron spin is a magnetic property. In most molecules, all electrons are paired, so for each "spin up" electron there is a "spin down" electron and their magnetic fields cancel out. When all electrons are paired, the molecule is diamagnetic meaning that it responds only weakly to a magnetic field.

If the electrons are not paired, they can adopt the same spin in the presence of a magnetic field. This accounts for the attraction of the paramagnetic molecule to the magnetic field. Therefore, for a molecule to be paramagnetic, it must have unpaired electrons. The correct molecular orbital energy level diagram for an O_2 molecule is shown in Fig. 7.

Figure 7
Molecular Orbital Energy Diagram
for Oxygen
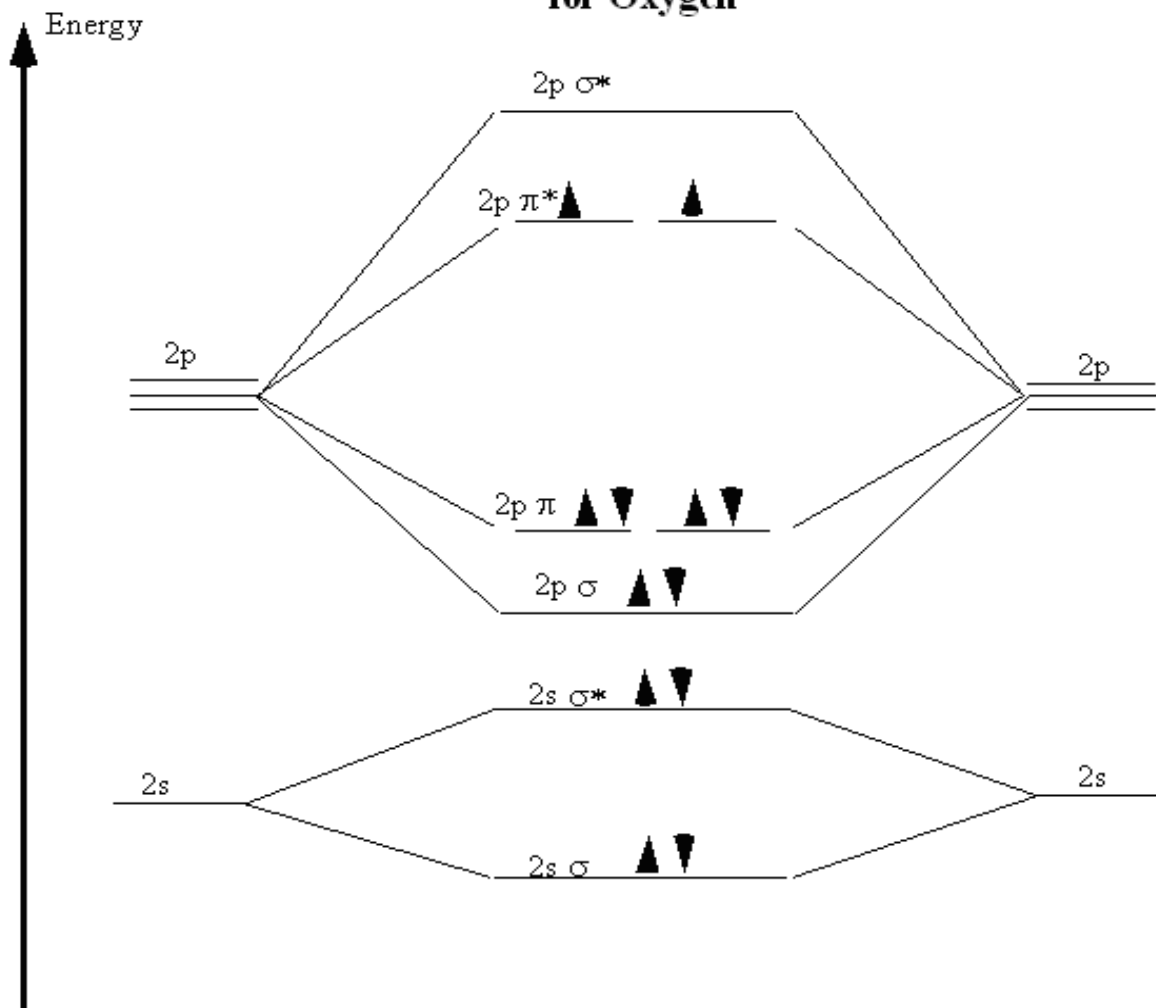
In comparing these three diatomic molecules, we recall that N_2 has the strongest bond, followed by O_2 and F_2. We have previously accounted for this comparison with Lewis structures, showing that N_2 is a triple bond, O_2 is a double bond, and F_2 is a single bond. The molecular orbital energy level diagrams in Figs. 5 to 7 cast a new light on this analysis. Note that, in each case, the number of bonding electrons in these molecules is eight. The difference in bonding is entirely due to the number of antibonding electrons: 2 for N_2 , 4 for O_2 , and six for F_2. Thus, the strength of a bond must be related to the relative numbers of bonding and antibonding electrons in the molecule. Therefore, we now define the bond order as

$$\text{BondOrder} = \tfrac{1}{2}(\# \text{ bonding electrons} - \# \text{ antibonding electrons})$$

Note that, defined this way, the bond order for N_2 is 3, for O_2 is 2, and for F_2 is 1, which agrees with our conclusions from Lewis structures. We conclude that we can predict the relative strengths of bonds by comparing bond orders.

Review and Discussion Questions

1. Why does an electron shared by two nuclei have a lower potential energy than an electron on a single atom? Why does an electron shared by two nuclei have a lower kinetic energy than an electron on a single atom? How does this sharing result in a stable molecule? How can this affect be measured experimentally?
2. Explain why the bond in an H_2 molecule is almost twice as strong as the bond in the H_2^+ ion. Explain why the H_2 bond is less than twice as strong as the H_2^+ bond.
3. Be_2 is not a stable molecule. What information can we determine from this observation about the energies of molecular orbitals?
4. Less energy is required to remove an electron from an F_2 molecule than to remove an electron from an F atom. Therefore, the energy of that electron is higher in the molecule than in the atom. Explain why, nevertheless, F_2 is a stable molecule, i.e., the energy of an F_2 molecule is less than the energy of two F atoms.
5. Why do the orbitals of an atom "hybridize" when forming a bond?
6. Calculate the bond orders of the following molecules and predict which molecule in each pair has the stronger bond:

    1. C_2 or C_2^+
    2. B_2 or B_2^+
    3. F_2 or F_2^-
    4. O_2 or O_2^+

7. Which of the following diatomic molecules are paramagnetic: CO, Cl_2, NO, N_2 ?

8. B_2 is observed to be paramagnetic. Using this information, draw an appropriate molecular orbital energy level diagram for B_2.

Energetics of Chemical Reactions

The Foundation

We begin our study of the energetics of chemical reactions with our understanding of mass relationships, determined by the stoichiometry of balanced reactions and the relative atomic masses of the elements. We will assume a conceptual understanding of energy based on the physics of mechanics, and in particular, we will assume the law of conservation of energy. In developing a molecular understanding of the reaction energetics, we will further assume our understanding of chemical bonding via valence shell electron pair sharing and molecular orbital theory.

Goals

The heat released or consumed in a chemical reaction is typically amongst the most easily observed and most readily appreciated consequences of the reaction. Many chemical reactions are performed routinely specifically for the purpose of utilizing the heat released by the reaction.

We are interested here in an understanding of the energetics of chemical reactions. Specifically, we wish to know what factors determine whether heat is absorbed or released during a chemical reaction. With that knowledge, we seek to quantify and predict the amount of heat anticipated in a chemical reaction. We expect to find that the quantity of heat absorbed or released during a reaction is related to the bonding of the molecules involved in the reaction.

Prior to answering these questions, we must first answer a few questions regarding the nature of heat. Despite our common familiarity with heat (particularly in Houston), the concept of heat is somewhat elusive to define. We recognize heat as "whatever it is that makes things hot," but this definition is too imprecise to permit measurement or any other conceptual progress. Exactly how do we define and measure heat?

Observation 1: Measurement of Heat by Temperature

We can define in a variety of ways a temperature scale which permits quantitative measurement of "how hot" an object is. Such scales are typically based on the expansion and contraction of materials, particularly of liquid mercury, or on variation of resistance in wires or thermocouples. Using such scales, we can easily show that heating an object causes its temperature to rise.

It is important, however, to distinguish between heat and temperature. These two concepts are not one and the same. To illustrate the difference, we begin by measuring the temperature rise produced by a given amount of heat, focusing on the temperature rise in 1000g of water produced by burning 1.0g of methane gas. We discover by performing this experiment repeatedly that the temperature of this quantity of water always rises by exactly 13.3°C. Therefore, the same quantity of heat must always be produced by reaction of this quantity of methane.

If we burn 1.0g of methane to heat 500g of water instead, we observe a temperature rise of 26.6°C. If we burn 1.0g of methane to heat 1000g of iron, we observe a temperature rise of 123°C. Therefore, the temperature rise observed is a function of the quantity of material heated as well as the nature of the material heated. Consequently, 13.3°C is not an appropriate measure of this quantity of heat, since we cannot say that the burning of 1.0g of methane "produces 13.3°C of heat." Such a statement is clearly revealed to be nonsense, so the concepts of temperature and heat must be kept distinct.

Our observations do reveal that we can relate the temperature rise produced in a substance to a fixed quantity of heat, provided that we specify the type and amount of the substance. Therefore, we define a property for each substance, called the **heat capacity**, which relates the temperature rise to the quantity of heat absorbed. We define q to be the quantity of heat, and $\Delta(T)$ to be the temperature rise produced by this heat. The heat capacity C is defined by
Equation:

$$q = C\Delta(T)$$

This equation, however, is only a definition and does not help us calculate either q or C, since we know neither one.

Next, however, we observe that we can also elevate the temperature of a substance **mechanically**, that is, by doing work on it. As simple examples, we can warm water by stirring it, or warm metal by rubbing or scraping it. (As an historical note, these observations were crucial in establishing that heat is equivalent to work in its effect on matter, demonstrating that heat is therefore a form of energy.) Although it is difficult to do, we can measure the amount of work required to elevate the temperature of 1g of water by 1°C. We find that the amount of work required is invariably equal to 4.184J. Consequently, adding 4.184J of energy to 1g of water must elevate the energy of the water molecules by an amount measured by 1°C. By conservation of energy, the energy of the water molecules does not depend on how that energy was acquired. Therefore, the increase in energy measured by a 1°C temperature increase is the same regardless of whether the water was heated or stirred. As such, 4.184J must also be the amount of energy added to the water molecules when they are **heated** by 1°C rather than stirred. We have therefore effectively measured the heat q required to elevate the temperature of 1g of water by 1°C. Referring back to [link], we now can calculate that the heat capacity of 1g of water must be $4.184\frac{J}{°C}$. The heat capacity **per gram** of a substance is referred to as the **specific heat** of the substance, usually indicated by the symbol c_s. The specific heat of water is $4.184\frac{J}{°C}$.

Determining the heat capacity (or specific heat) of water is an extremely important measurement for two reasons. First, from the heat capacity of water we can determine the heat capacity of any other substance very simply. Imagine taking a hot 5.0g iron weight at 100°C and placing it in 10.0g of water at 25°C. We know from experience that the iron bar will be cooled and the water will be heated until both have achieved the same temperature. This is an easy experiment to perform, and we find that the final temperature of the iron and water is 28.8°C. Clearly, the temperature of the water has been raised by 3.8°C. From [link] and the specific heat of water, we can calculate that the water must have absorbed an amount of heat $q = (10.0g)\left(\left(4.184\frac{J}{g°C}\right)\right)(3.8°C) = 159J$. By conservation of

energy, this must be the amount of heat **lost** by the 1g iron weight, whose temperature was lowered by 71.2°C. Again referring to [link], we can calculate the specific heat of the iron bar to be
$c_s = \frac{-159J}{(-71.2°C)(5.0g)} = 0.45\frac{J}{g°C}$. Following this procedure, we can easily produce extensive tables of heat capacities for many substances.

Second, and perhaps more importantly for our purposes, we can use the known specific heat of water to measure the heat released in any chemical reaction. To analyze a previous example, we observed that the combustion of 1.0g of methane gas released sufficient heat to increase the temperature of 1000g of water by 13.3°C. The heat capacity of 1000g of water must be
$(1000g)\left(4.184\frac{J}{g°C}\right) = 4184\frac{J}{°C}$. Therefore, by [link], elevating the temperature of 1000g of water by 13.3°C must require $55,650J = 55.65$ kJ of heat. Therefore, burning 1.0g of methane gas produces exactly 55.65kJ of heat.

The method of measuring reaction energies by capturing the heat evolved in a water bath and measuring the temperature rise produced in that water bath is called **calorimetry**. This method is dependent on the equivalence of heat and work as transfers of energy, and on the law of conservation of energy. Following this procedure, we can straightforwardly measure the heat released or absorbed in any easily performed chemical reaction. For reactions which are difficult to initiate or which occur only under restricted conditions or which are exceedingly slow, we will require alternative methods.

Observation 2: Hess' Law of Reaction Energies

Hydrogen gas, which is of potential interest nationally as a clean fuel, can be generated by the reaction of carbon (coal) and water:
Equation:

$$C(s) + 2H_2O(g) \rightarrow CO_2(g) + 2H_2(g)$$
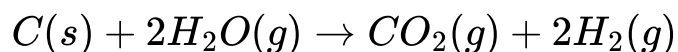
Calorimetry reveals that this reaction requires the **input** of 90.1kJ of heat for every mole of $C(s)$ consumed. By convention, when heat is absorbed during a reaction, we consider the quantity of heat to be a positive number: in chemical terms, $q > 0$ for an **endothermic** reaction. When heat is evolved, the reaction is **exothermic** and $q < 0$ by convention.

It is interesting to ask where this input energy goes when the reaction occurs. One way to answer this question is to consider the fact that the reaction converts one fuel, $C(s)$, into another, $H_2(g)$. To compare the energy available in each fuel, we can measure the heat evolved in the combustion of each fuel with one mole of oxygen gas. We observe that
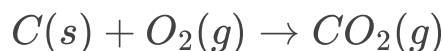**Equation:**

$$C(s) + O_2(g) \rightarrow CO_2(g)$$
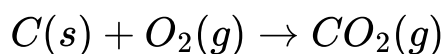
produces 393.5kJ for one mole of carbon burned; hence $q = -393.5\,\text{kJ}$. The reaction
Equation:

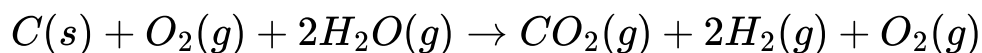$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$
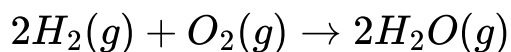
produces 483.6kJ for two moles of hydrogen gas burned, so $q = -483.6\,\text{kJ}$. It is evident that more energy is available from combustion of the hydrogen fuel than from combustion of the carbon fuel, so it is not surprising that conversion of the carbon fuel to hydrogen fuel requires the input of energy.

Of considerable importance is the observation that the heat input in [link], 90.1kJ, is exactly equal to the **difference** between the heat evolved, -393.5kJ, in the combustion of carbon and the heat evolved, -483.6kJ, in the combustion of hydrogen. This is not a coincidence: if we take the combustion of carbon and add to it the **reverse** of the combustion of hydrogen, we get

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

$$2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$$

Equation:

$$C(s) + O_2(g) + 2H_2O(g) \rightarrow CO_2(g) + 2H_2(g) + O_2(g)$$

Canceling the $O_2(g)$ from both sides, since it is net neither a reactant nor product, [link] is equivalent to [link]. Thus, taking the combustion of carbon and "subtracting" the combustion of hydrogen (or more accurately, adding the reverse of the combustion of hydrogen) yields [link]. And, the heat of the combustion of carbon **minus** the heat of the combustion of hydrogen equals the heat of [link].

By studying many chemical reactions in this way, we discover that this result, known as **Hess' Law**, is general.
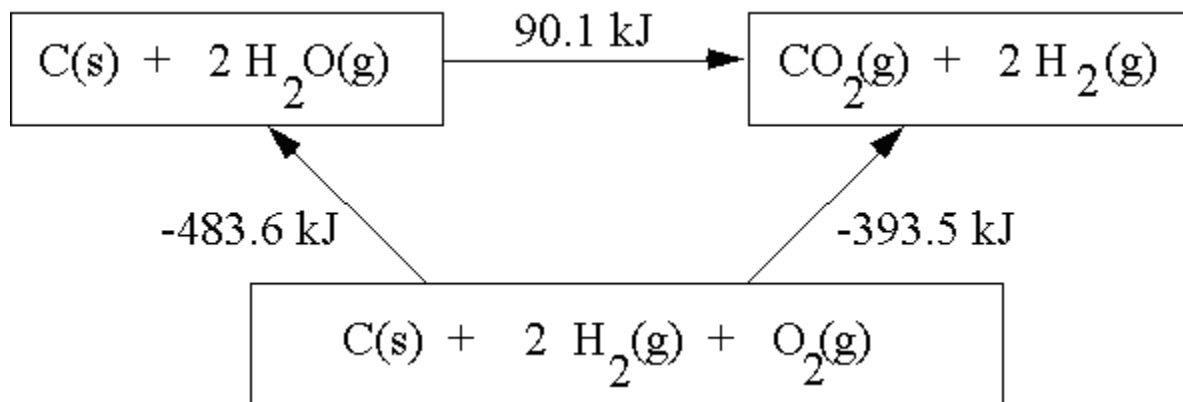Hess' Law

The heat of any reaction is equal to the sum of the heats of reaction for any set of reactions which in sum are equivalent to the overall reaction.

(Although we have not considered the restriction, applicability of this law requires that all reactions considered proceed under similar conditions: we will consider all reactions to occur at constant pressure.)

A pictorial view of Hess' Law as applied to the heat of [link] is illustrative. In [link], the reactants $C(s) + 2H_2O(g)$ are placed together in a box, representing the **state** of the materials involved in the reaction prior to the reaction. The products $CO_2(g) + 2H_2(g)$ are placed together in a second box representing the state of the materials involved after the reaction. The reaction arrow connecting these boxes is labeled with the heat of this reaction. Now we take these same materials and place them in a third box containing $C(s)$, $O_2(g)$, and $2H_2(g)$. This box is connected to the reactant and product boxes with reaction arrows, labeled by the heats of reaction in [link] and [link].
A Pictorial View of Hess' Law

This picture of Hess' Law reveals that the heat of reaction along the "path" directly connecting the reactant state to the product state is exactly equal to the total heat of reaction along the alternative "path" connecting reactants to products via the intermediate state containing $C(s)$, $O_2(g)$, and $2H_2(g)$. A consequence of our observation of Hess' Law is therefore that the net heat evolved or absorbed during a reaction is independent of the path connecting the reactant to product. (This statement is again subject to our restriction that all reactions in the alternative path must occur under constant pressure conditions.)

A slightly different view of [link] results from beginning at the reactant box and following a complete circuit through the other boxes leading back to the reactant box, summing the net heats of reaction as we go. We discover that the net heat transferred (again provided that all reactions occur under constant pressure) is exactly zero. This is a statement of the conservation of energy: the energy in the reactant state does not depend upon the processes which produced that state. Therefore, we cannot extract any energy from the reactants by a process which simply recreates the reactants. Were this not the case, we could endlessly produce unlimited quantities of energy by following the circuitous path which continually reproduces the initial reactants.

By this reasoning, we can define an energy function whose value for the reactants is independent of how the reactant state was prepared. Likewise, the value of this energy function in the product state is independent of how the products are prepared. We choose this function, H, so that the change in the function, $\Delta(H) = H_{\text{products}} - H_{\text{reactants}}$, is equal to the heat of

reaction q under constant pressure conditions. H, which we call the **enthalpy**, is a **state function**, since its value depends only on the state of the materials under consideration, that is, the temperature, pressure and composition of these materials.

The concept of a state function is somewhat analogous to the idea of elevation. Consider the difference in elevation between the first floor and the third floor of a building. This difference is independent of the path we choose to get from the first floor to the third floor. We can simply climb up two flights of stairs, or we can climb one flight of stairs, walk the length of the building, then walk a second flight of stairs. Or we can ride the elevator. We could even walk outside and have a crane lift us to the roof of the building, from which we climb down to the third floor. Each path produces exactly the same elevation gain, even though the distance traveled is significantly different from one path to the next. This is simply because the elevation is a "state function." Our elevation, standing on the third floor, is independent of how we got to the third floor, and the same is true of the first floor. Since the elevation thus a state function, the elevation gain is independent of the path.

Now, the existence of an energy state function H is of considerable importance in calculating heats of reaction. Consider the prototypical reaction in [link], with reactants R being converted to products P. We wish to calculate the heat absorbed or released in this reaction, which is $\Delta(H)$. Since H is a state function, we can follow any path from R to P and calculate $\Delta(H)$ along that path. In [link], we consider one such possible path, consisting of two reactions passing through an intermediate state containing all the atoms involved in the reaction, each in elemental form. This is a useful intermediate state since it can be used for any possible chemical reaction. For example, in [link], the atoms involved in the reaction are C, H, and O, each of which are represented in the intermediate state in elemental form. We can see in [link] that the $\Delta(H)$ for the overall reaction is now the difference between the $\Delta(H)$ in the formation of the products P from the elements and the $\Delta(H)$ in the formation of the reactants R from the elements.

Calculation of ΔH
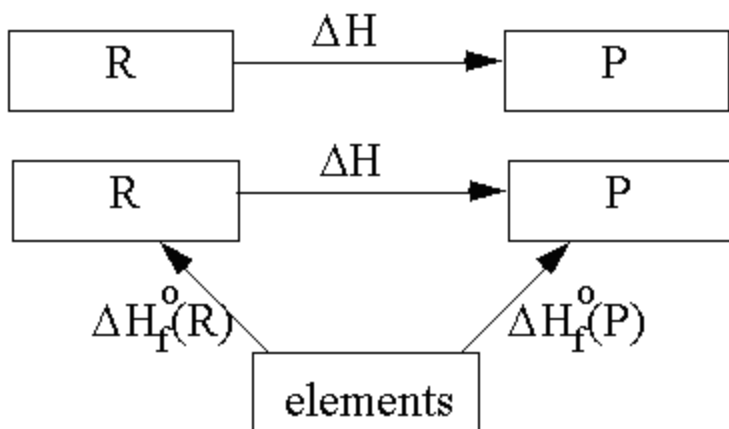
The $\Delta(H)$ values for formation of each material from the elements are thus of general utility in calculating $\Delta(H)$ for any reaction of interest. We therefore define the **standard formation reaction** for reactant R, as

$$\text{elements in standard state} \to R$$

and the heat involved in this reaction is the **standard enthalpy of formation**, designated by $\Delta\left(\overset{\circ}{H_f}\right)$. The subscript f, standing for "formation," indicates that the $\Delta(H)$ is for the reaction creating the material from the elements in standard state. The superscript $^\circ$ indicates that the reactions occur under constant standard pressure conditions of 1 atm. From [link], we see that the heat of any reaction can be calculated from **Equation:**

$$\Delta\left(\overset{\circ}{H_f}\right) = \Delta\left(\overset{\circ}{H_{f \text{ products}}}\right) - \Delta\left(\overset{\circ}{H_{f \text{ reactants}}}\right)$$

Extensive tables of $\Delta\left(\overset{\circ}{H_f}\right)$ have been compiled and published. This allows us to calculate with complete confidence the heat of reaction for any reaction of interest, even including hypothetical reactions which may be difficult to perform or impossibly slow to react.

Observation 3: Bond Energies in Polyatomic Molecules

The **bond energy** for a molecule is the energy required to separate the two bonded atoms to great distance. We recall that the total energy of the bonding electrons is lower when the two atoms are separated by the bond distance than when they are separated by a great distance. As such, the energy input required to separate the atoms elevates the energy of the electrons when the bond is broken.

We can use diatomic bond energies to calculate the heat of reaction $\Delta(H)$ for any reaction involving only diatomic molecules. We consider two simple examples. First, the reaction
**Equation:**

$$H_2(g) + \text{Br}(g) \rightarrow H(g) + H\,\text{Br}(g)$$
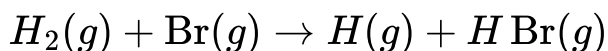
is observed to be endothermic with heat of reaction $70\frac{\text{kJ}}{\text{mol}}$. Note that this reaction can be viewed as consisting entirely of the breaking of the H_2 bond followed by the formation of the $H\,\text{Br}$ bond. Consequently, we must input energy equal to the bond energy of H_2 ($436\frac{\text{kJ}}{\text{mol}}$), but in forming the $H\,\text{Br}$ bond we recover output energy equal to the bond energy of $H\,\text{Br}$ ($366\frac{\text{kJ}}{\text{mol}}$). Therefore the heat of [link] at constant pressure must be equal to difference in these bond energies, $70\frac{\text{kJ}}{\text{mol}}$.

Now we can answer the question, at least for this reaction, of where the energy "goes" during the reaction. The reason this reaction absorbs energy is that the bond which must be broken, H_2, is stronger than the bond which is formed, $H\,\text{Br}$. Note that energy is released when the $H\,\text{Br}$ bond is formed, but the amount of energy released is less than the amount of energy required to break the H_2 bond in the first place.

The second example is similar:
Equation:

$$H_2(g) + \text{Br}_2(g) \rightarrow 2H\,\text{Br}(g)$$
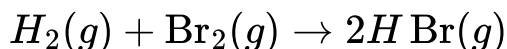
This reaction is exothermic with $\Delta \left(H^{\circ} \right) = -103 \frac{\text{kJ}}{\text{mol}}$. In this case, we must break an H_2 bond, with energy $436 \frac{\text{kJ}}{\text{mol}}$, and a Br_2 bond, with energy $193 \frac{\text{kJ}}{\text{mol}}$. Since two $H\,Br$ molecules are formed, we must form two $H\,Br$ bonds, each with bond energy $366 \frac{\text{kJ}}{\text{mol}}$. In total, then, breaking the bonds in the reactants requires $629 \frac{\text{kJ}}{\text{mol}}$, and forming the new bonds releases $732 \frac{\text{kJ}}{\text{mol}}$, for a net release of $103 \frac{\text{kJ}}{\text{mol}}$. This calculation reveals that the reaction is exothermic because, although we must break one very strong bond and one weaker bond, we form two strong bonds.

There are two items worth reflection in these examples. First, energy is released in a chemical reaction due to the **formation** of strong bonds. Breaking a bond, on the other hand, always requires the **input** of energy. Second, [link] does not actually proceed by the two-step process of breaking both reactant bonds, thus forming four free atoms, followed by making two new bonds. The actual process of the reaction is significantly more complicated. The details of this process are irrelevant to the energetics of the reaction, however, since, as we have shown, the heat of reaction $\Delta(H)$ does not depend on the path of the reaction. This is another example of the utility of Hess' law.

We now proceed to apply this bond energy analysis to the energetics of reactions involving polyatomic molecules. A simple example is the combustion of hydrogen gas discussed previously here. This is an explosive reaction, producing 483.6kJ per mole of oxygen. Calculating the heat of reaction from bond energies requires us to know the bond energies in H_2O. In this case, we must break not one but two bonds:
Equation:

$$H_2O(g) \rightarrow 2H(g) + O(g)$$
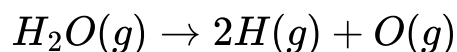
The energy required to perform this reaction is measured to be $926.9 \frac{\text{kJ}}{\text{mol}}$. [link] can proceed by a path in which we first break two H_2 bonds and one O_2 bond, then we follow the reverse of [link] twice:
Equation:

$$2H_2(g) + O_2(g) \rightarrow 4H(g) + 2O(g)$$

$$4H(g) + 2O(g) \rightarrow 2H_2O(g)$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$
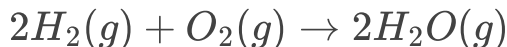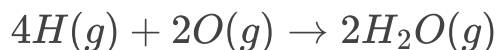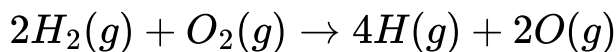
Therefore, the energy of [link] must be the energy required to break two H_2 bonds and one O_2 bond minus twice the energy of [link]. We calculate that $\Delta(H^\circ) = 2 \times \left(436\frac{\text{kJ}}{\text{mol}}\right) + 498.3\frac{\text{kJ}}{\text{mol}} - 2 \times \left(926.9\frac{\text{kJ}}{\text{mol}}\right) = -483.5\frac{\text{kJ}}{\text{mol}}$. It is clear from this calculation that [link] is strongly exothermic because of the very large amount of energy released when two hydrogen atoms and one oxygen atom form a water molecule.

It is tempting to use the heat of [link] to calculate the energy of an O-H bond. Since breaking the two O-H bonds in water requires $926.9\frac{\text{kJ}}{\text{mol}}$, then we might infer that breaking a single O-H bond requires $\frac{926.9\frac{\text{kJ}}{\text{mol}}}{2} = 463.5\frac{\text{kJ}}{\text{mol}}$. However, the reaction

Equation:

$$H_2O(g) \rightarrow OH(g) + H(g)$$

has $\Delta(H^\circ) = 492\frac{\text{kJ}}{\text{mol}}$. Therefore, the energy required to break an O-H bond in H_2O is not the same as the energy required to break the O-H bond in the OH diatomic molecule. Stated differently, it requires more energy to break the first O-H bond in water than is required to break the second O-H bond.

In general, we find that the energy required to break a bond between any two particular atoms depends upon the molecule those two atoms are in. Considering yet again oxygen and hydrogen, we find that the energy required to break the O-H bond in methanol (CH_3OH) is $437\frac{\text{kJ}}{\text{mol}}$, which differs substantially from the energy of [link]. Similarly, the energy required to break a single C-H bond in methane (CH_4) is $435\frac{\text{kJ}}{\text{mol}}$, but the energy required to break all four C-H bonds in methane is $1663\frac{\text{kJ}}{\text{mol}}$, which is not equal to four times the energy of one bond. As another such comparison,

the energy required to break a C-H bond is $400\frac{\text{kJ}}{\text{mol}}$ in trichloromethane ($HCCl_3$), $414\frac{\text{kJ}}{\text{mol}}$ in dichloromethane (H_2CCl_2), and $422\frac{\text{kJ}}{\text{mol}}$ in chloromethane (H_3CCl).

These observations are somewhat discouraging, since they reveal that, to use bond energies to calculate the heat of a reaction, we must first measure the bond energies for all bonds for all molecules involved in that reaction. This is almost certainly more difficult than it is desirable. On the other hand, we can note that the bond energies for similar bonds in similar molecules are close to one another. The C-H bond energies in the three chloromethanes above illustrate this quite well. We can estimate the C-H bond energy in any one of these chloromethanes by the average C-H bond energy in the three chloromethanes molecule, which is $412\frac{\text{kJ}}{\text{mol}}$. Likewise, the average of the C-H bond energies in methane is $\frac{1663\frac{\text{kJ}}{\text{mol}}}{4} = 416\frac{\text{kJ}}{\text{mol}}$ and is thus a reasonable approximation to the energy required to break a single C-H bond in methane.

By analyzing many bond energies in many molecules, we find that, in general, we can approximate the bond energy in any particular molecule by the average of the energies of similar bonds. These average bond energies can then be used to estimate the heat of a reaction without measuring all of the required bond energies.

Consider for example the combustion of methane to form water and carbon dioxide:
Equation:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$
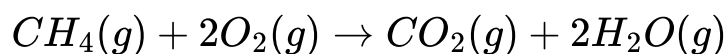
We can estimate the heat of this reaction by using average bond energies. We must break four C-H bonds at an energy cost of approximately $4 \times 412\frac{\text{kJ}}{\text{mol}}$ and two O_2 bonds at an energy cost of approximately $2 \times 496\frac{\text{kJ}}{\text{mol}}$. Forming the bonds in the products releases approximately $2 \times 743\frac{\text{kJ}}{\text{mol}}$ for the two C=O double bonds and $4 \times 463\frac{\text{kJ}}{\text{mol}}$ for the O-H bonds. Net, the heat of reaction is thus approximately

$\Delta(H^\circ) = 1648 + 992 - 1486 - 1852 = -698 \frac{\text{kJ}}{\text{mol}}$. This is a rather rough approximation to the actual heat of combustion of methane, $-890 \frac{\text{kJ}}{\text{mol}}$. Therefore, we cannot use average bond energies to predict accurately the heat of a reaction. We can get an estimate, which may be sufficiently useful. Moreover, we can use these calculations to gain insight into the energetics of the reaction. For example, [link] is strongly exothermic, which is why methane gas (the primary component in natural gas) is an excellent fuel. From our calculation, we can see that the reaction involved breaking six bonds and forming six new bonds. The bonds formed are substantially stronger than those broken, thus accounting for the net release of energy during the reaction.

Review and Discussion Questions

Exercise:

Problem:

Assume you have two samples of two different metals, X and Z. The samples are exactly the same mass.

Both samples are heated to the same temperature. Then each sample is placed into separate glasses containing identical quantities of cold water, initially at identical temperatures below that of the metals. The final temperature of the water containing metal X is greater than the final temperature of the water containing metal Z. Which of the two metals has the larger heat capacity? Explain your conclusion.

If each sample, initially at the same temperature, is heated with exactly 100J of energy, which sample has the higher final temperature?
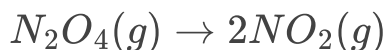
Exercise:

Problem:

Explain how Hess' Law is a consequence of conservation of energy.

Exercise:

Problem:

Consider the reaction

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

Draw Lewis structures for each of N_2O_4 and NO_2. On the basis of these structures, predict whether the reaction is endothermic or exothermic, and explain your reasoning.

Exercise:

Problem:

Why is the bond energy of H_2 not equal to $\Delta\left(H_f^{\,\circ}\right)$ of H_2? For what species is the enthalpy of formation related to the bond energy of H_2?

Exercise:

Suggest a reason why $\Delta\left(H^{\,\circ}\right)$ for the reaction

$$CO_2(g) \rightarrow CO(g) + O(g)$$

is not equal to $\Delta\left(H^{\,\circ}\right)$ for the reaction

Problem:
$$CO(g) \rightarrow C(g) + O(g)$$

Exercise:

Problem:

Determine whether the reaction is exothermic or endothermic for each of the following circumstances:

The heat of combustion of the products is greater than the heat of combustion of the reactants.

The enthalpy of formation of the products is greater than the enthalpy of formation of the reactants.

The total of the bond energies of the products is greater than the total of the bond energies for the reactants.